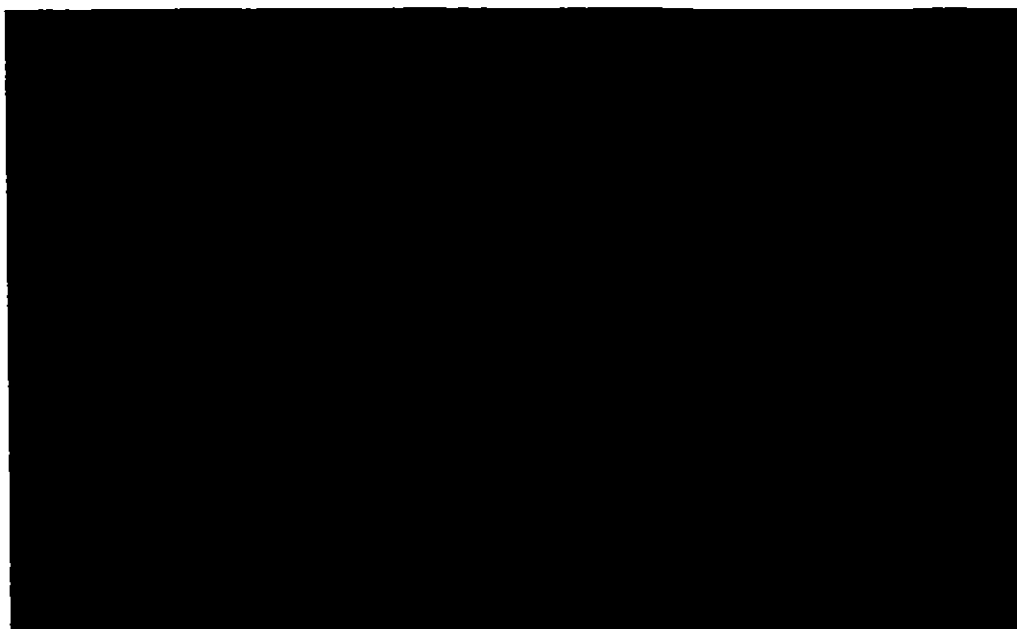




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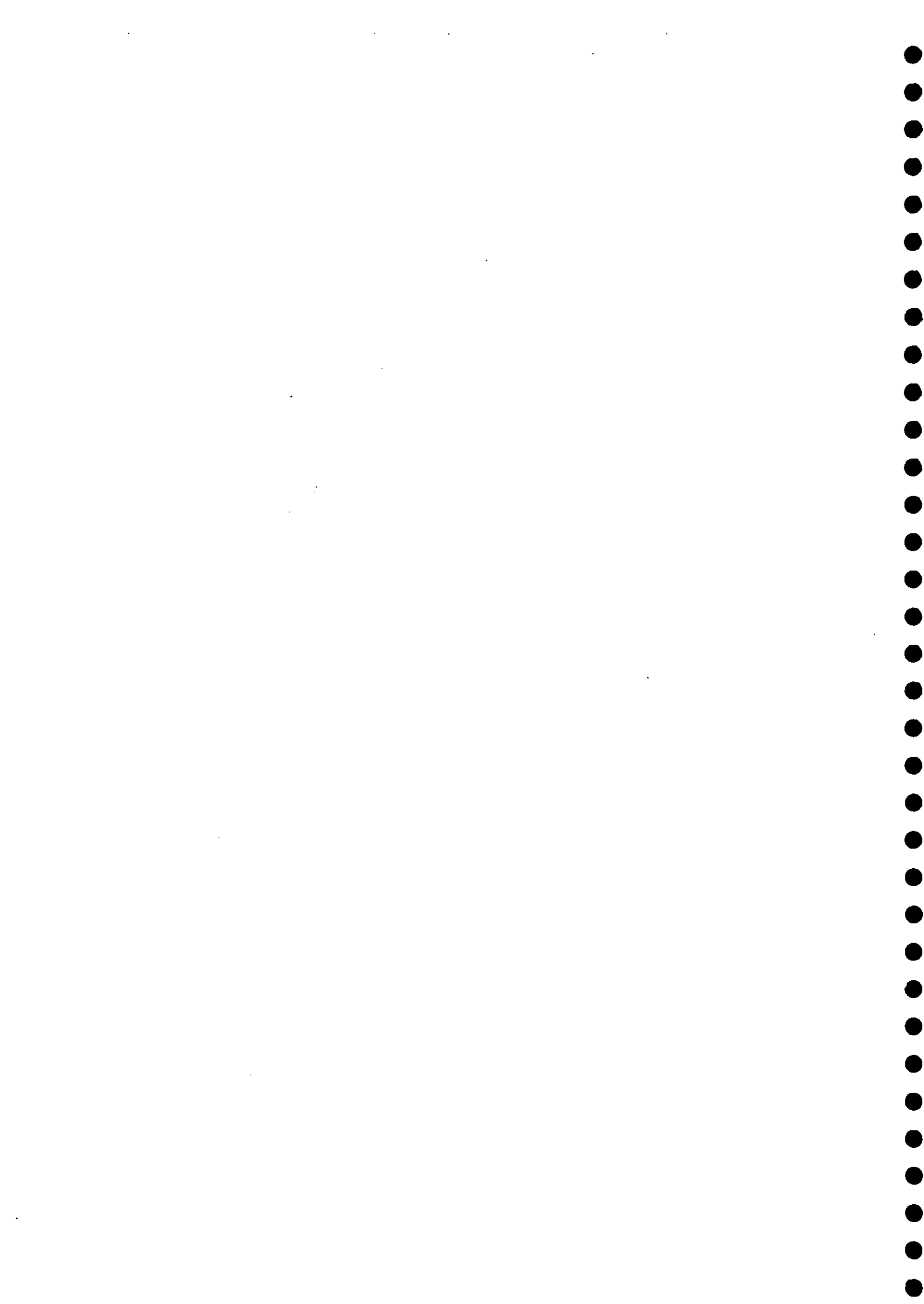
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REVERSIBILITY OF ACIDIFICATION IN WALES

Prepared Under Contract to National Power

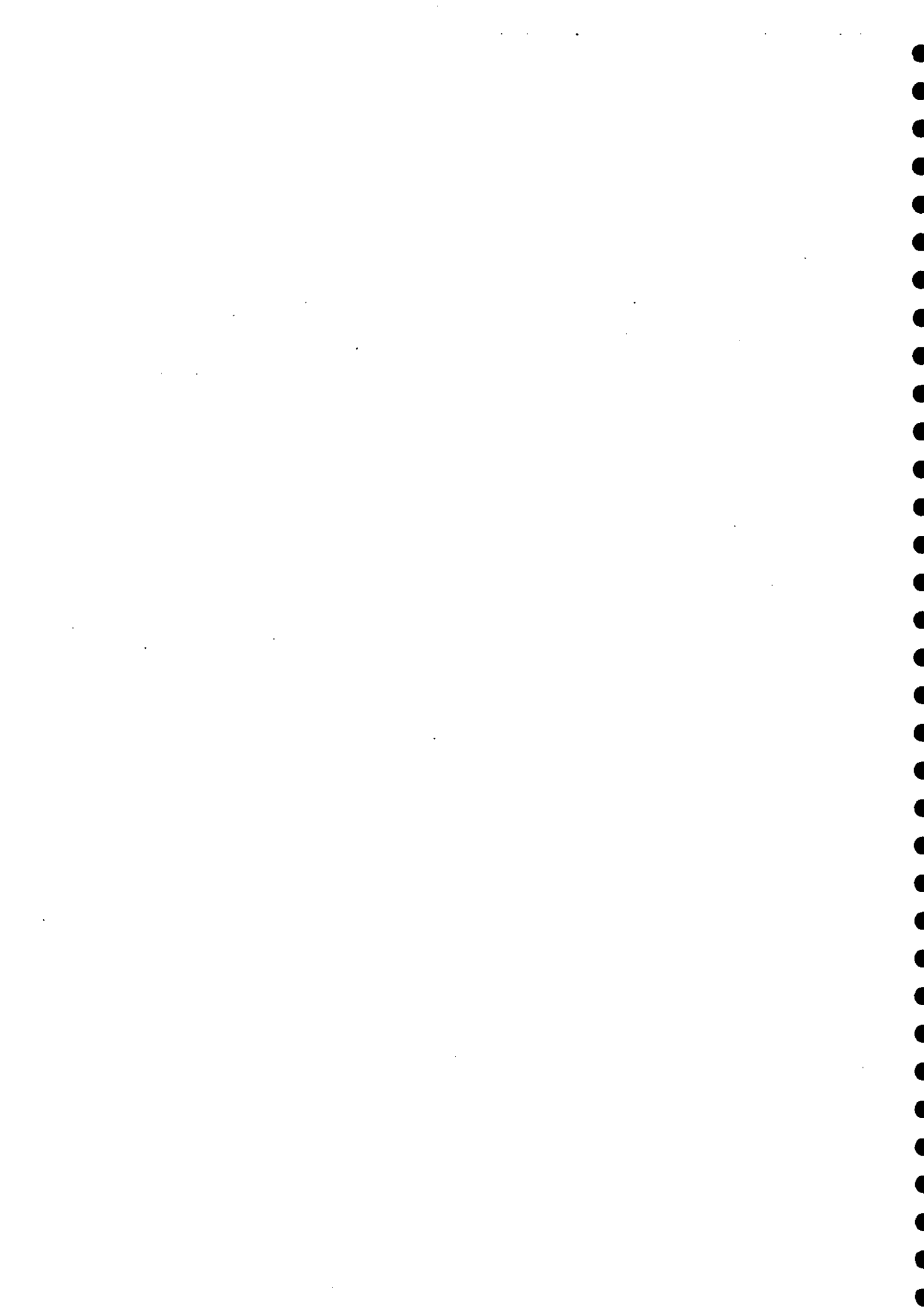
By

Alan Jenkins and Daniel Butterfield



EXECUTIVE SUMMARY

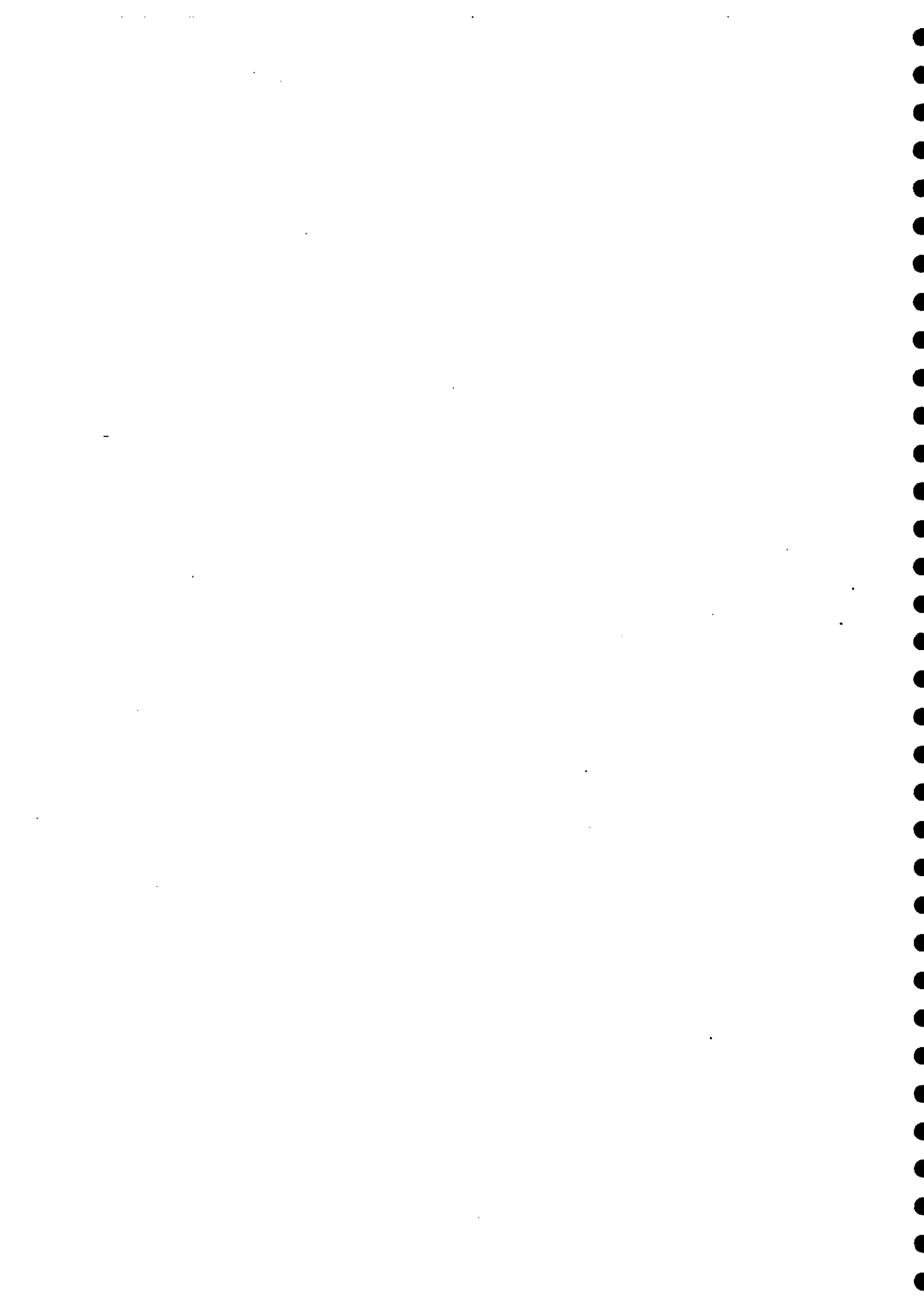
The MAGIC model has been applied in its regional mode to simulate surface water chemistry in Wales. The calibrated model is utilised to perform six, fifty year forecasts under different deposition reduction scenarios. The results indicate that under the reductions outlined in the Large Combustion Plant Directive, the most heavily acidified waters in the region will increase in alkalinity but not all will achieve positive alkalinity. If deposition reductions of 100% are made on present day levels, around 95% will have positive alkalinity. Conversely, if reductions of only 20% are made continued acidification will occur and only 50% of waters will show positive alkalinity. Model sensitivity analysis, at a single catchment in the region, indicates that background (pre-acidification) sulphate deposition and organic content does not greatly influence predicted alkalinity although the results must be interpreted in the light of other model assumptions used.



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1. INTRODUCTION

Acidic deposition, acidification of surface waters and loss of fish populations occur over large regions of northern Europe and America. International negotiations to reduce the emissions of acidifying compounds (SO_2 and NO_x) to the atmosphere are intended to mitigate the adverse environmental effects of these acids. The UK has agreed to a 30% reduction of SO_2 emissions relative to the 1980 level by 1993 and further reductions are anticipated in future years as outlined under the Large Combustion Plant Directive (LCPD).

The geographical and temporal links between emissions and transport, deposition and aquatic ecosystem impacts are complex and non-linear. The application of mathematical models of surface water acidification in conjunction with data from regional surveys of surface water chemistry can be an important tool in the assessment of the likely benefits of acidic deposition reduction. A regionalisation procedure based on the conceptual model MAGIC (Model of Acidification of Groundwater In Catchments) has been developed that allows forecasts of water quality changes in response to alternate deposition reduction scenarios. The regional modelling procedure is used to produce a weighted ensemble of model simulations whose output variables have statistical properties that match those of measured chemical variables obtained from a synoptic survey of 130 lakes and streams in Wales in 1984. This survey was based upon weekly sampling of surface waters throughout the year and was undertaken by the Welsh Water Authority.

The calibrated model is then used to analyze changes in the distributions of water quality variables over the period 1984 to 2034. The model predictions for this period are driven by observed deposition chemistry from a number of monitoring sites in south and mid-Wales between 1984 and 1990 and, thereafter, deposition reduction scenarios based around the LCPD.

2. THE MAGIC MODEL

MAGIC consists of: (1) a section in which the concentration of major ions are assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution/precipitation/speciation of aluminium and dissolution/speciation of inorganic carbon; and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time due to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change in surface water acidity thus depends both on flux factors and the inherent characteristics of the impacted soils.

Sulphate adsorption is treated in the model by a Langmuir isotherm. Aluminium dissolution/precipitation is assumed to be

controlled by equilibrium with a solid phase of $\text{Al}(\text{OH})_3$. Aluminium speciation is calculated by considering hydrolysis reactions as well as complexation with sulphate and fluoride. Speciation of inorganic carbon is computed from known equilibrium equations. Cation exchange is also treated using equilibrium (Gaines-Thomas) equations. Weathering rates are assumed to be constant with time in the model. Finally, a set of mass balance equations for the base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long term reconstructions of surface water chemistry (Cosby et al. 1985a, b, c).

3. MODEL APPLICATION AND ASSUMPTIONS

Details of the regional model methodology, model application, and data used are given in Jenkins et al. (1990) which is reproduced in its entirety in appendix A of this report. The assumptions made in this analysis are detailed in Jenkins et al. (1990). Due to problems with computer software and the need to improve on the previous application, however, the original regional model was re-calibrated and some of the original assumptions were changed. Those most relevant to this application are;

(i) There is no organic component in either soil or soilwater in the regional model. This is necessary since TOC data for surface water was not reported in the water quality survey. The presence

of organics in the model will tend to give lower background pH and so may affect predicted future chemistry. The effect of organic anions in these systems is assessed on a site specific basis and is reported in section 6.

(ii) Aluminium is controlled by an assumed equilibrium with gibbsite with selectivity set at 8.6. Aluminium precipitation in the stream is allowed (i.e. not as stated in the paper by Jenkins et al. 1990). This change was effected to standardise the regional model application with other regional and site specific applications.

(iii) Background sulphate input (wet plus dry) is assumed to be at sea-salt ratio (constant through time) plus 1.5 ueq l^{-1} to account for volcanic sources. This factor will also affect stream chemistry in simulated background and future predictions and again, is assessed using a site specific sensitivity analysis (see section 6).

(iv) The Large Combustion Plant Directive (LCPD) is based upon agreed reductions in sulphur emissions and the link between changes in emissions and deposition is a difficult one. This application assumes a simple link between emission and deposition such that a 20% decrease in emissions will produce a 20% decrease in deposition in Wales. The link between emissions reduction and deposition reduction is not straight forward, however, and relevant atmospheric transport models would need to be applied to quantify the decrease in emissions required to give a certain

deposition reduction in any given area. This, in essence, is the basis of the Critical Loads approach, that is, working backwards from the pollution levels a receptor will tolerate to identifying the emissions reduction needed to achieve that deposition level.

4. OBSERVED AND SIMULATED WATER CHEMISTRY DISTRIBUTIONS

The model produces a good match between the observed and simulated present day water chemistry distributions. Observed and predicted frequency distributions are shown in figures 1a - 1i (potassium is not included since concentrations are uniformly low) and statistical indices of the two populations are given in tables 1a - 1i.

Chloride (Table 1g and Figure 1g) produces the closest match between observed and predicted and this is expected since this ion acts conservatively in the model. Similarly, sulphate (Table 1h and Figure 1h) may be assumed to be essentially at steady state in acidified catchments and so also demonstrates a good match. Nitrate (Table 1i and Figure 1i) is not considered in the model except as a first order uptake (i.e. a loss from the soil - soilwater system through biomass accumulation) and the small discrepancy between observed and predicted is unimportant. In any case, the observed data is rather poor quality, reported only as TON. All base cation (Tables 1d - 1f and Figures 1d - 1f) and the alkalinity (Table 1b and Figure 1b) distributions demonstrate good matches.

Both aluminium (Table 1c and Figure 1c) and hydrogen (Table 1a and Figure 1a) observed and simulated frequency distributions show a slight discrepancy at the extreme of the distribution. This is caused by just one simulation which predicts a very high aluminium associated with a relatively low hydrogen concentration. The implication is that the Gibbsite selectivity value of 8.6 is inappropriate in this one case. It must be stressed that this represents just one simulation in the total of 252 successful calibrations. Furthermore, it is possible that such an extreme chemistry may exist in the region but was not sampled. The simulation is included in the model since aluminium and hydrogen concentrations are not used to constrain model selection.

As a further comment on the validity of the model application and goodness of fit, the biological indicators of water quality were assessed to determine the percentage of sites at which pH was less than 5.2, alkalinity less than zero and calcium concentration less than 50 ueq l⁻¹. For pH, 46% of waters were observed to be below 5.2 compared with a predicted 37%. For calcium, 2% observed compares well with the 5% predicted below 50 ueq l⁻¹, and predicted alkalinity less than zero of 31% compares with the observed 48%.

5. SIMULATED WATER CHEMISTRY DISTRIBUTIONS UNDER DEPOSITION REDUCTION SCENARIOS

To establish the LCPD scenario for the regional model, bearing in mind that the observed survey data was collected in 1984, the observed deposition data for Llyn Brianne for 1984 - 1989 was used (Donald et al. 1990 and unpublished data) and is shown in figure 2. Between 1984 and 1989, sulphate deposition has been relatively constant at a level of approximately 15 kg ha^{-1} . This represents a decrease of about 25% on 1980 levels. The LCPD aims to achieve a 20% reduction on 1980 levels by 1993 and clearly, this has already been achieved. The LCPD scenario utilised for the model forecasts in this study incorporates a further 20% reduction on the 1984 level by 1993. In this respect, even the base LCPD scenario may be assumed to represent a "best case" with respect to recovery of surface waters and the water chemistry effects of the true LCPD scenario will fall somewhere between runs 1 and 6 (see later). The deposition reductions considered for this study are given in table 2 and figure 3 as percent reductions in sulphate deposition from present day levels.

Predicted water chemistry distributions are shown as;

(i) A sequence of cumulative frequency curves for each assumed deposition reduction scenario and each major ion (Figures 4 - 9 for runs 1 - 6, respectively), showing the change in distribution through time with curves for 1984 (simulated, 1994, 2004 and 2034).

(ii) The percentage of surface waters not achieving broad chemical criteria; that is, calcium concentration less than 50 $\mu\text{eq l}^{-1}$, negative alkalinity and pH less than 5.2 (Table 3). These criteria are commonly used to identify the suitability of freshwaters for maintaining viable brown trout populations. The degree of recovery of surface waters across the region is summarised as;

(i) Box and whisker diagrams summarising the predicted regional response of each major ion under the 6 deposition reduction scenarios (Appendix B).

(ii) Summary statistics, including mean, standard deviation, variance, 5 and 95 percentiles, maximum and minimum, of the predicted distribution of each ion in 2034 (Appendix C) for each deposition reduction scenario.

(iii) Frequency distributions of simulated 1984 and 2034 chemistry for each ion (Appendix D).

RUN 1 (LCPD); Sulphate concentrations (Figure 4d) in surface waters are substantially reduced across the region with both a shift in mean and the extreme (high) end of the distribution. This is associated with a similar decrease in calcium (Figure 4e) and magnesium (Figure 4f), as expected from mobile anion theory, although the sodium (Figure 4g) distribution remains almost constant since this ion is dominated by sea-salt inputs to the systems and the model forecasts assume that chloride inputs

remain unchanged in the future. As a result, alkalinity (Figure 4a) improves slightly at the extreme negative end of the distribution (i.e. those sites with very large negative alkalinity improve substantially). This recovery, however, is slow to take effect. In response to the 20% reduction in deposition over the first 10 years of the simulation, there is little response. By 2004, however, the alkalinity response is rapid following the 60% decrease. Hydrogen (Figure 4c) and aluminium (Figure 4b) concentrations, on the other hand, decrease rapidly in response to the changes in sulphate flux through the system. The model suggests, therefore, that as sulphate is reduced the cations respond to maintain charge neutrality. Consequently, concentrations of base cations and acidic cations (H and Al) decrease in proportions dictated by the F-factors of the systems. The F-factor is a function of the ability of systems to neutralise acid anions with base cations and so may be related to the base saturation of the soils. The apparent shift in alkalinity at only the negative extreme of the distribution implies that recovery is most significant where the soils have been heavily impacted and current F-factors are very low. i.e. a decrease in strong acid anions is associated with a decrease in H and Al concentrations and so alkalinity improves. This is supported by the relationship between change in alkalinity (2034 - 1984) and base saturation (Figure 10) which shows that those sites which have continued to lose alkalinity exhibit the lowest soil base saturation. There is, however, considerable scatter. At the positive alkalinity sites, decreases in strong acid anion are associated with decreases in base cations, since these sites

have relatively high F-factors, and so alkalinity remains approximately the same.

RUN 2 ("best" scenario); This scenario, 100% decrease in deposition by 2004, produces a complete shift in the predicted alkalinity (Figure 5a) distribution indicating increased alkalinity at all sites. Al (Figure 5b) and H⁺ (Figure 5c) are reduced to very low concentrations across the region.

RUN 3; This scenario addresses a similar 60% decrease to RUN 1 but assumes that this is achieved by 1998 rather than 2004. The overall change in chemistry by 2004 is very similar to RUN 1 but there is little predicted change between 2004 and 2034 (Figures 6a - 6g). This implies that the chemical changes in surface waters will occur rapidly following changes in deposition but the timing of the deposition reduction is not important compared to the absolute amount of reduction.

RUN 4 and RUN 5; These scenarios fall within RUNS 1 and 2 achieving total deposition reductions of 90% (RUN 4) and 70 (RUN 3). Results from RUN 4 are given in figures 7a - 7g and RUN 5 in figures 8a - 8g.

RUN 6 ("worst" case); This scenario assumes that the 20% decrease by 1993 is the only deposition reduction achieved. The results of the simulation (Figures 9a - 9g) show that this is not enough to prevent further acidification across the region. The alkalinity (Figure 9a) distribution shifts towards the low end

and Al (Figure 9b) and H⁺ (Figure 9c) concentrations increase.

The biological relevance of increased water acidity stems from the evidence of declining fish populations and changing invertebrate distributions. Field and laboratory studies have indicated that a pH of 5.5, calcium concentration of 50 $\mu\text{eq l}^{-1}$ and inorganic aluminium concentration of 20 $\mu\text{g l}^{-1}$ are key biological thresholds (Brown 1983, Harriman et al. 1987). These quantities are strongly correlated (high aluminium levels are usually found with low pH and low calcium) and the toxicity of each individual chemical is uncertain. Table 3 indicates the percentage of surface waters which for each simulation and every 10 years of that simulation, fall below similar criteria, including pH and calcium but also alkalinity since a value of zero is commonly used to determine critical loads for surface waters.

6. SENSITIVITY TO BACKGROUND SULPHATE DEPOSITION AND ORGANICS

Sensitivity was assessed by applying the MAGIC model in site-

specific mode. The model was calibrated as; (i) a best fit to observed present day data using the assumptions for background SO_4 input (zero) and organics (zero) utilised in the regional analysis; (ii) a model with identical parameter values to (i) but including an additional 15 ueq l^{-1} excess SO_4 in background input; (iii) a model with identical parameter values to (i) but including 300 mmol m^{-3} organic matter in soil and stream water; (iv) a model with identical parameter values to (i) but including both the higher background SO_4 input and organics. A fuzzy optimisation technique was used to calibrate the MAGIC model to each of the four cases and the Nant Y Gronwen catchment, a moorland catchment in Mid-Wales was used as the base-case.

The calibrations were carried out in a sequential manner. First the concentrations of the stream Cl and SO_4 were calibrated by adjusting dry deposition of sea salts and gaseous/particulate S compounds under the assumption that these ions are in approximate steady-state with respect to atmospheric inputs. Next, the NO_3 and NH_4 concentrations were calibrated by adjusting first-order uptake functions to match observed surface water concentrations. Finally, the base cation concentrations were calibrated using an optimisation procedure based on the Rosenbrock (1960) algorithm.

The base-cation calibration involved fitting the results of long-term model simulations to currently observed water and soil base-cation data (the target variables). The target variables consisted of surface water concentrations of Ca, Mg, Na and K and soil exchangeable fractions of Ca, Mg, Na and K. The target

variables thus comprise a vector of measured values all of which must be reproduced by the model if a calibration is to be considered successful.

Those physico-chemical soil and surface water characteristics measured in the field were considered "fixed" parameters in the model and the measurements were directly used in the models during the calibration procedure. These included; soil depth, bulk density, cation exchange capacity, and runoff. Base cation weathering rates and base-cation exchange selectivity coefficients for the soils are not directly measurable and were used as "adjustable" model parameters to be optimized in the calibration procedure.

The calibrations were performed on simulations run from 1849 to 1989 (cf. 1844 - 1984 for the regional analysis). The historical SO_4 deposition sequence used was exactly as the regional analysis and with four years of observation at the site appended. After each historical simulation, the model variables in 1989 were compared with observations in 1989; the adjustable parameters were modified as necessary to improve the fit; the historical simulation was re-run; the procedure was repeated until no further improvement in the fit was achieved.

Because the measurement of the fixed parameters and the target variables are subject to errors, a "fuzzy" optimisation calibration procedure was used. This consisted of multiple calibrations of each model structure using perturbations of the

values of the fixed parameters and estimated uncertainties of the target variables. The sizes of the perturbations of the fixed parameters were based on known measurement errors or spatial variability of the parameters. The uncertainties in the target variables were estimated as the measurement errors of the variables; $5 \text{ } \mu\text{eq l}^{-1}$ for concentrations of surface water variables and 0.5% for soil base saturation variables.

Each of the multiple calibrations began with; (i) a random selection of perturbed values of the fixed parameters; (ii) a random selection of the starting values of the adjustable parameters; and (iii) specification of uncertainty in the target variables. The adjustable parameters were then optimized using the Rosenbrock algorithm to achieve a minimum error fit to the target variables. The optimization algorithm was stopped and the calibration considered complete when the simulated values of all target variables were within the pre-specified uncertainty limits for the observations. This procedure was undertaken ten times for each of the four models.

Using the fuzzy optimization based on multiple calibrations, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values which were simulated given the specified uncertainty in the fixed parameter values and measured target variables. Figures 11a and 11b show the forecast simulations for the four model structures and for constant SO_4

deposition at present levels (a) and a 40% decrease in deposition by 2003 and held constant at that level thereafter (b). The degree of overlap between the simulated 1989 and predicted 2039 alkalinity concentrations indicate that the model predictions are not influenced by background SO_4 deposition assumptions. The model calibration responds to increased background SO_4 deposition by utilising a greater capacity for the soil to adsorb SO_4 such that present day chemistry can still be achieved by the model. This is intuitively correct and could be corroborated through field measurements. The regional model, therefore, provides for less SO_4 adsorption than may occur in reality but this does not apparently bias the predicted alkalinity recovery. High organic concentrations have some small influence on alkalinity (Figure x) leading to slightly greater recovery in surface water alkalinity. This is probably the result of the organic matter dissociation constants applied to the very high organic content. Since the dissociation is pH related, the relatively small change in pH caused by the reduced deposition scenario decreases the organic anion concentration and so slightly increases the alkalinity through charge balance principles. The implication is that if such high organic concentrations are found in Welsh surface waters then the regional predictions reported earlier may be biased towards demonstrating less recovery. On the other hand, this analysis predicts that the bias is of the order of 5 - 10 ueq l^{-1} .

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Table 1. Descriptive statistics for the observed and simulated 1984 water chemistry distributions. (a) hydrogen, (b) alkalinity, (c) aluminium, (d) sodium, (e) calcium, (f) magnesium, (g) chloride, (h) sulphate and (i) nitrate.

Table 2. Percentage reductions in sulphate deposition.

Table 3. Percentage of surface waters failing to achieve biologically relevant chemical "thresholds" for each of the deposition reduction scenarios; (a) calcium less than 50 ueq l⁻¹, (b) alkalinity less than zero and (c) pH less than 5.2.

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Figure 1. Observed and simulated 1984 water chemistry distributions; (a) hydrogen, (b) alkalinity, (c) aluminium, (d) sodium, (e) calcium, (f) magnesium, (g) chloride, (h) sulphate and (i) nitrate.

Figure 2. Observed wet deposition of sulphate in the Llyn Brianne area, mid-Wales, 1980 - 1989.

Figure 3. Future deposition reduction scenarios.

Figure 4. Cumulative frequency distributions of water chemistry for RUN 1; (a) alkalinity, (b) aluminium, (c) hydrogen, (d) sulphate, (e) calcium, (f) magnesium and (g) sodium.

Figure 5. Cumulative frequency distributions of water chemistry for RUN 2; (order of ions as in figure 4).

Figure 6. Cumulative frequency distributions of water chemistry for RUN 3; (order of ions as in figure 4).

Figure 7. Cumulative frequency distributions of water chemistry for RUN 4; (order of ions as in figure 4).

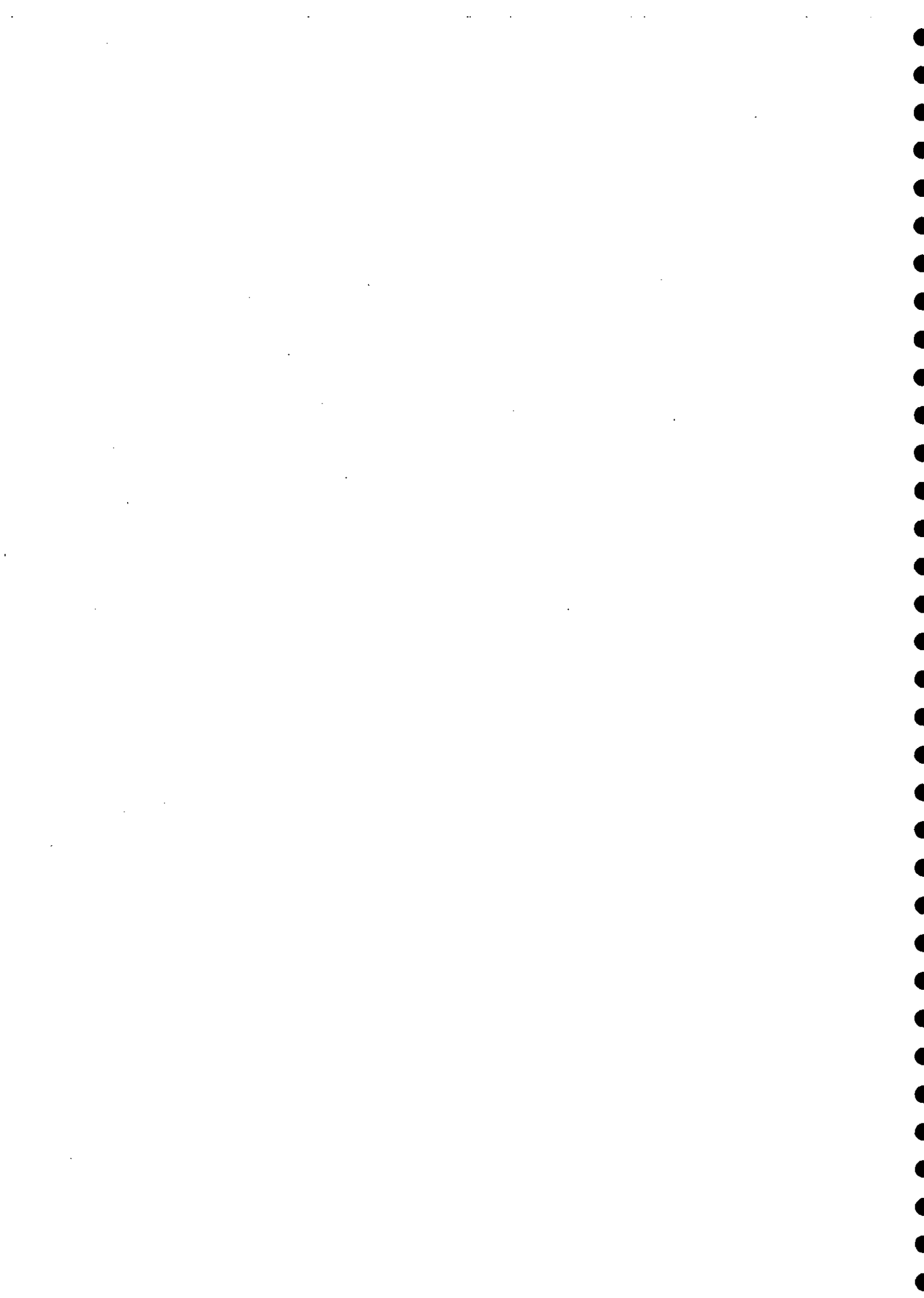
Figure 8. Cumulative frequency distributions of water chemistry for RUN 5; (order of ions as in figure 4).

Figure 9. Cumulative frequency distributions of water chemistry

for RUN 6; (order of ions as in figure 4).

Figure 10. Change in alkalinity (2035 simulated - 1985 simulated) against 1985 simulated percent base saturation for Run 1 (LCPD).

Figure 11. Comparison of simulated 1989 and 2039 alkalinity concentrations at the Nant Y Gronwen, Mid Wales, under constant future deposition (a) and 40% reduction (b).



Descriptive statistics for the observed and simulated water chemistry distributions.

Table 1a: Hydrogen.

	Observed 1984	Simulated 1984
Mean:	7.23	12.31
Standard Deviation:	11.32	9.57
Variance:	128.17	91.69
5 Percentile:	0.32	0.40
95 Percentile:	31.32	45.87
Maximum:	64.73	57.40
Minimum:	0.24	0.30

Table 1b: Alkalinity.

	Observed 1984	Simulated 1984
Mean:	2.94	-1.32
Standard Deviation:	46.56	28.99
Variance:	2167.52	840.41
5 Percentile:	-91.87	-91.04
95 Percentile:	68.77	69.49
Maximum:	89.76	86.60
Minimum:	-140.60	-138.40

Table 1c: Aluminium.

	Observed 1984	Simulated 1984
Mean:	10.84	8.38
Standard Deviation:	9.79	10.01
Variance:	95.89	100.16
5 Percentile:	3.33	0.00
95 Percentile:	27.50	43.79
Maximum:	68.89	82.90
Minimum:	1.11	0.00

Table 1d: Sodium.

	Observed 1984	Simulated 1984
Mean:	201.29	205.90
Standard Deviation:	27.90	16.33
Variance:	778.52	266.62
5 Percentile:	160.33	170.40
95 Percentile:	250.87	261.25
Maximum:	289.57	294.80
Minimum:	149.13	152.10

Table 1e: Calcium.

	Observed 1984	Simulated 1984
Mean:	106.62	103.93
Standard Deviation:	36.94	22.31
Variance:	1364.43	497.82
5 Percentile:	52.89	48.89
95 Percentile:	171.91	169.44
Maximum:	208.58	201.90
Minimum:	40.42	36.60

Table 1f: Magnesium.

	Observed 1984	Simulated 1984
Mean:	86.41	87.24
Standard Deviation:	19.9	14.82
Variance:	396.04	219.59
5 Percentile:	54.09	50.66
95 Percentile:	121.14	121.48
Maximum:	143.92	159.80
Minimum:	44.43	39.80

Table 1g: Chloride.

	Observed 1984	Simulated 1984
Mean:	244.11	246.38
Standard Deviation:	37.57	23.02
Variance:	1411.63	529.70
5 Percentile:	191.98	198.33
95 Percentile:	306.05	319.69
Maximum:	365.48	379.20
Minimum:	166.67	175.80

Table 1h: Sulphate.

	Observed 1984	Simulated 1984
Mean:	137.92	138.34
Standard Deviation:	38.01	22.23
Variance:	1444.92	494.24
5 Percentile:	66.17	70.44
95 Percentile:	188.63	202.29
Maximum:	277.33	284.90
Minimum:	49.14	51.80

Table 1i: Nitrate.

	Observed 1984	Simulated 1984
Mean:	20.44	25.52
Standard Deviation:	12.03	7.52
Variance:	144.65	56.50
5 Percentile:	7.39	9.30
95 Percentile:	40.90	51.07
Maximum:	59.52	69.80
Minimum:	7.142	2.30

Table 2. Percentage reductions in sulphate deposition.

Year	Run Number					
	1	2	3	4	5	6
1993	20	20	20	20	20	20
1998	40	60	60	60	50	20
2003	60	100	60	90	70	20

% Ca < 50 uEq/l

	Run Number					
Year	1	2	3	4	5	6
1984	5.2	5.2	5.2	5.2	5.2	5.2
1994	8.3	8.3	8.3	8.3	8.3	7.9
2004	11.1	17.9	11.1	16.7	12.7	7.9
2014	14.3	20.6	14.7	19.4	15.5	8.3
2024	14.7	23.0	14.7	19.8	16.3	8.3
2034	15.5	23.4	15.5	20.2	16.3	9.9

% Alkalinity < 0 uEq/l

	Run Number					
Year	1	2	3	4	5	6
1984	30.9	30.9	30.9	30.9	30.9	30.9
1994	32.5	31.8	31.8	31.8	32.1	31.8
2004	28.9	20.2	27.8	22.2	27.8	32.9
2014	24.2	12.3	23.0	14.7	20.6	34.9
2024	23.0	10.3	22.6	12.7	18.7	38.5
2034	23.0	9.9	21.8	11.9	18.3	39.7

% pH >< 5.2

	Run Number					
Year	1	2	3	4	5	6
1984	36.5	36.5	36.5	36.5	36.5	36.5
1994	37.7	37.7	37.7	37.7	37.7	37.7
2004	36.1	28.2	33.7	29.0	33.3	38.9
2014	32.9	17.5	31.3	21.8	28.6	41.3
2024	32.1	14.7	31.0	17.5	25.0	42.1
2034	31.7	13.5	30.2	17.5	24.6	44.4



Figure 1 (a)

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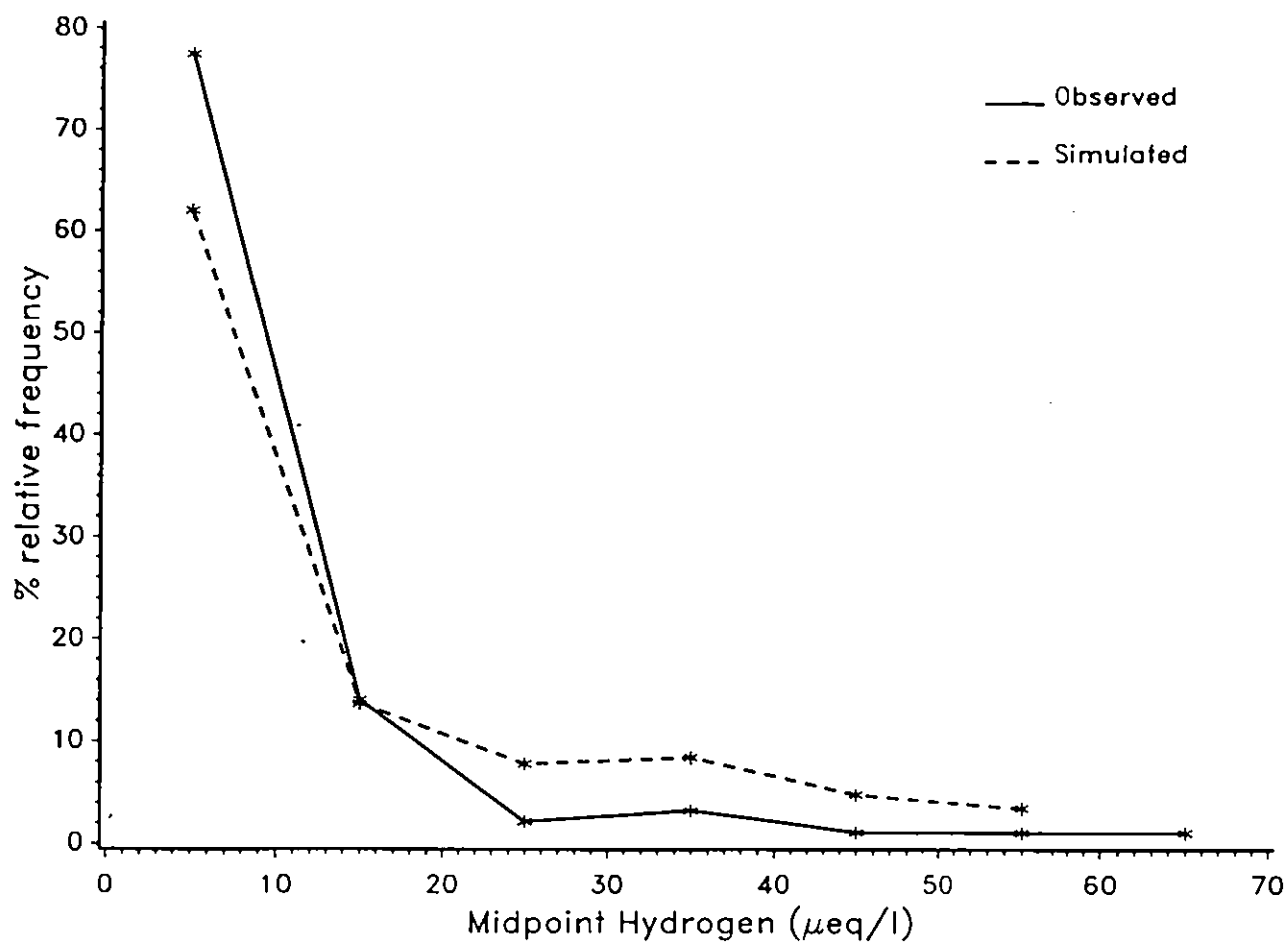


Figure 1 (b)

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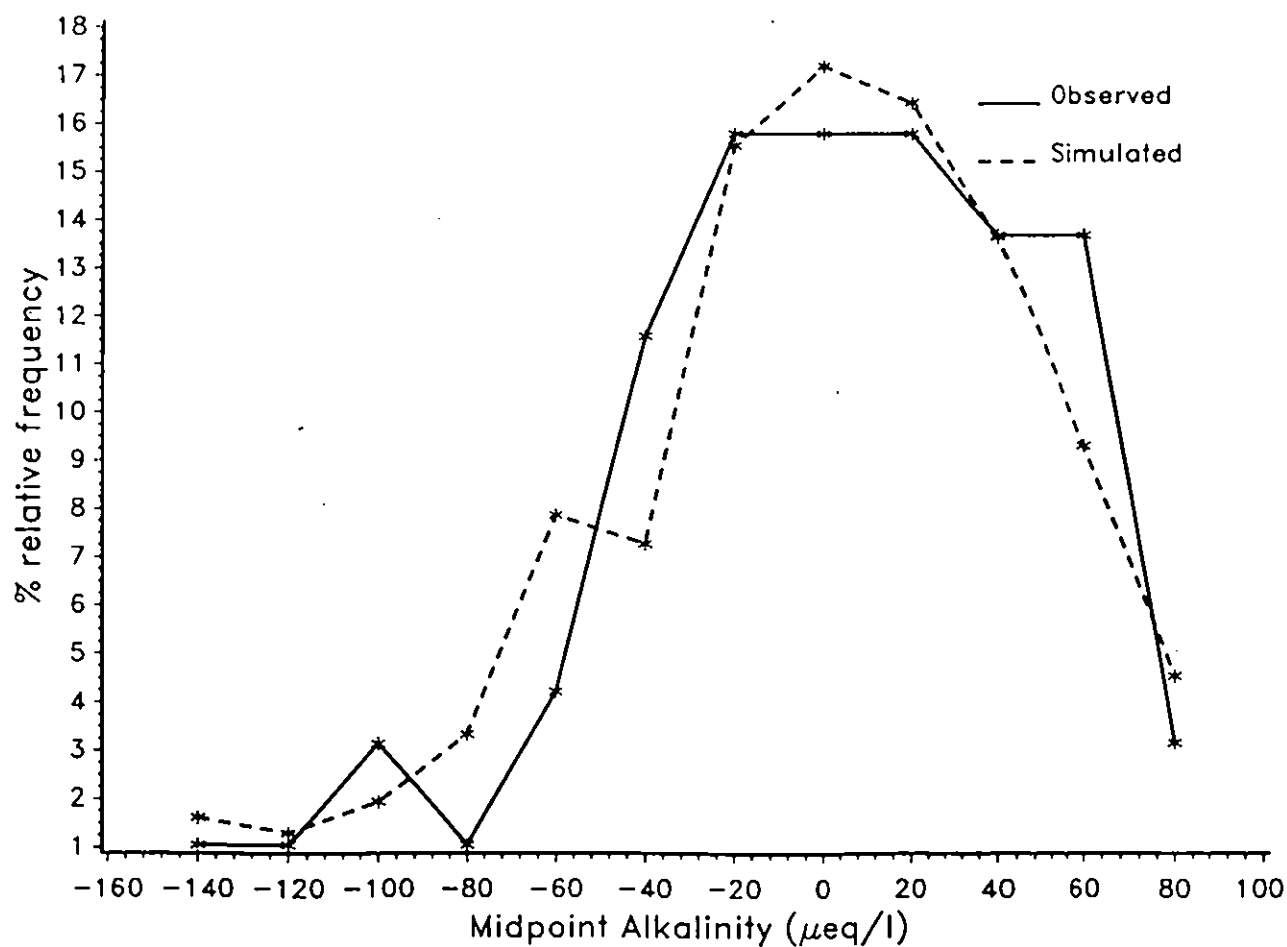


Figure 1 (c)

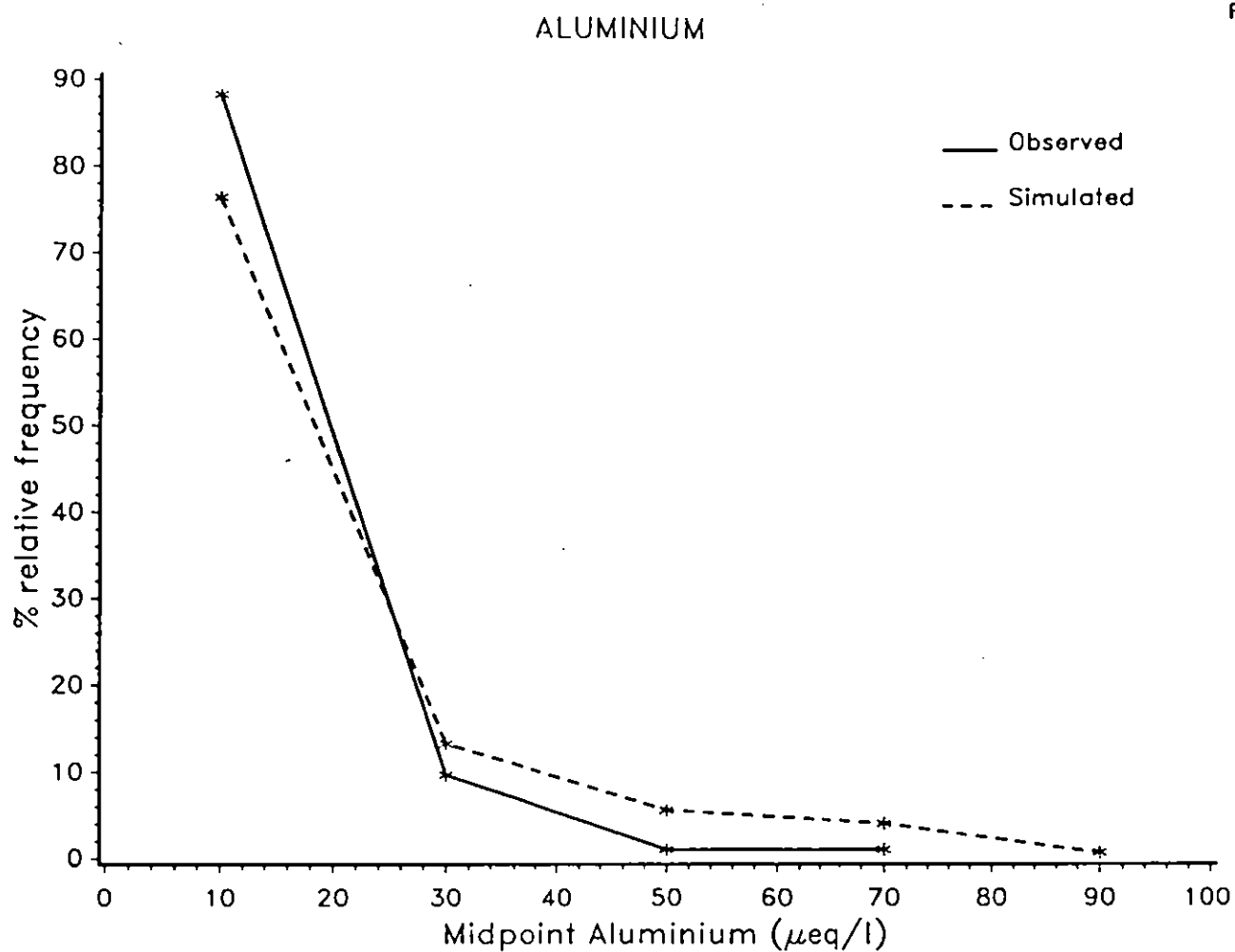
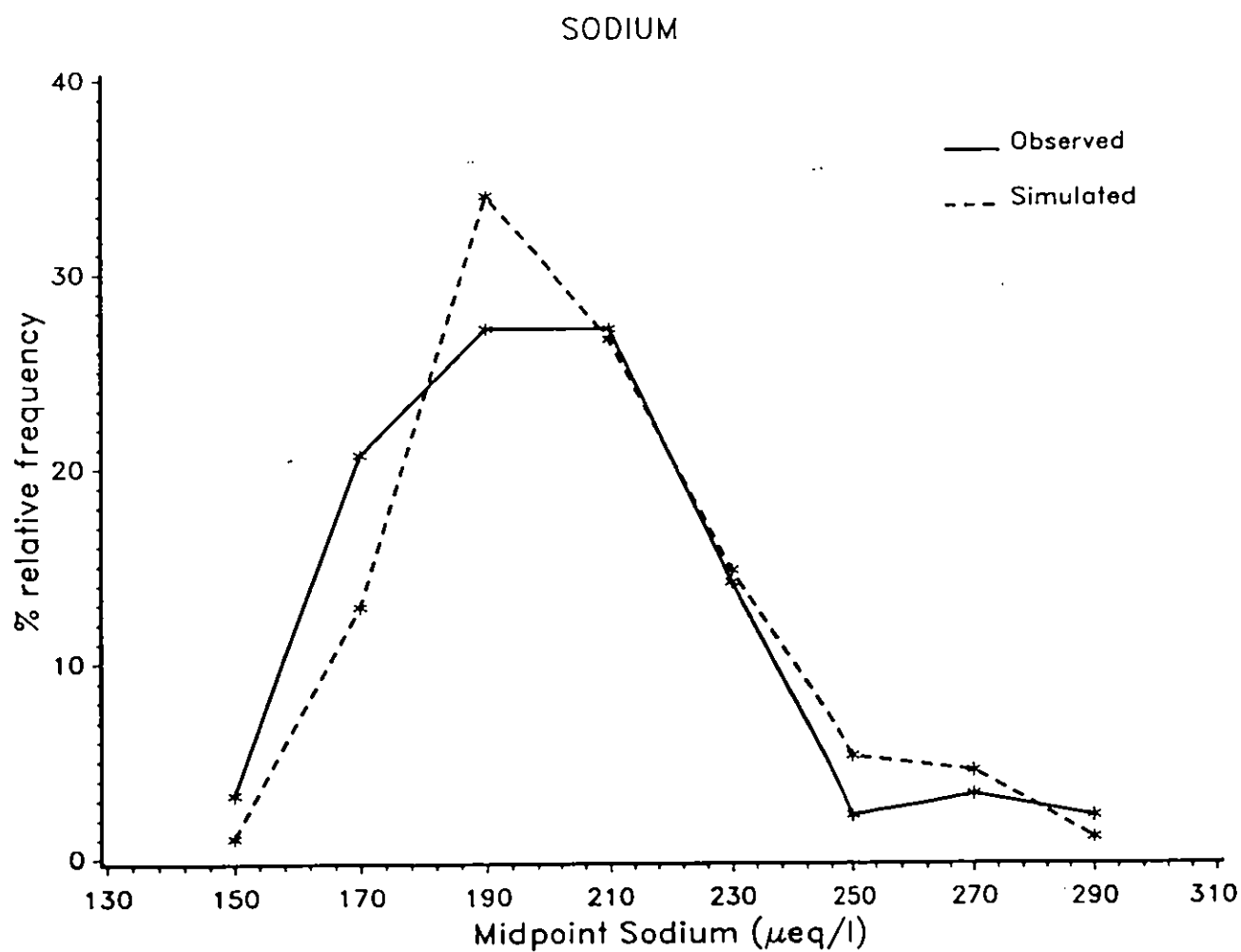
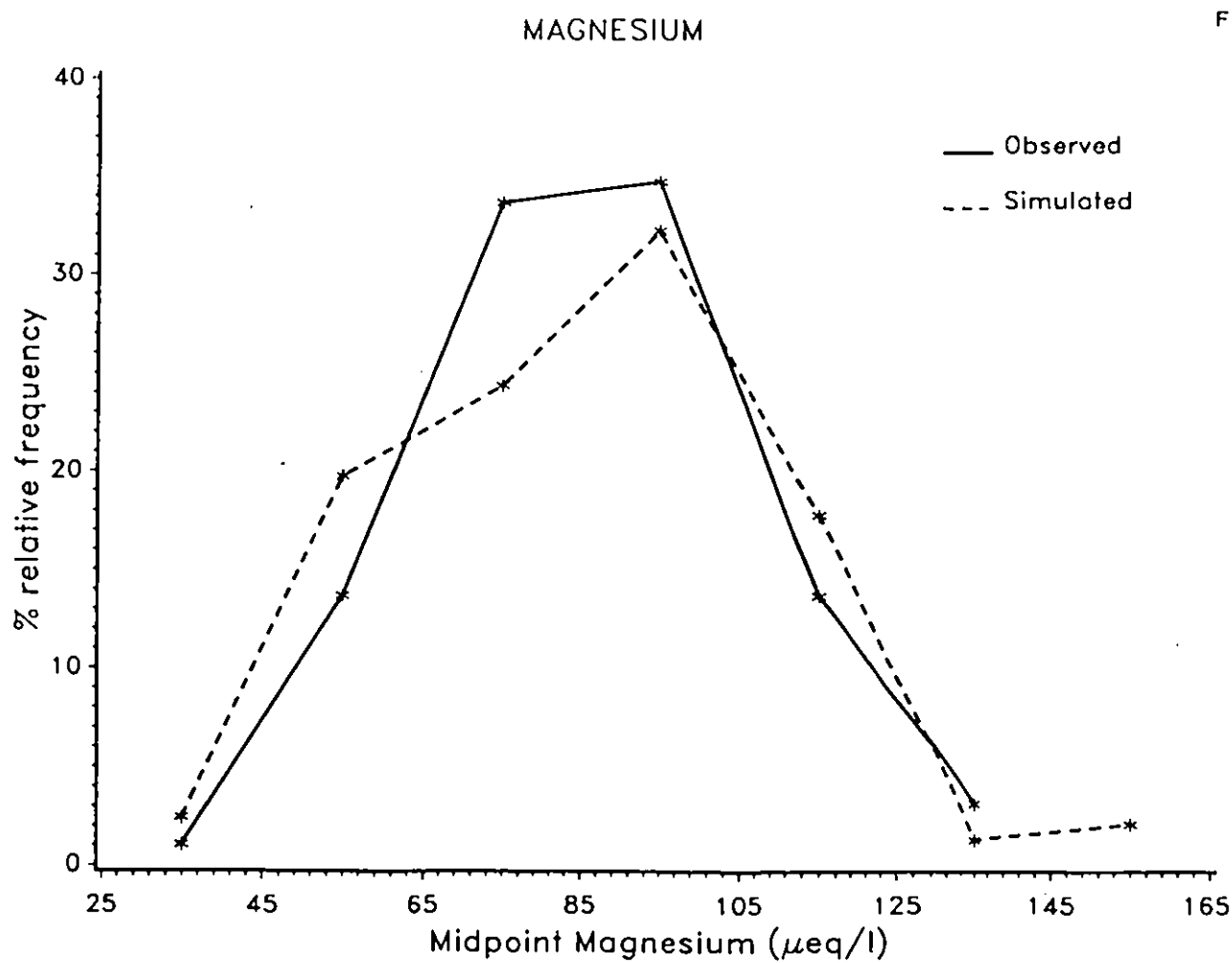
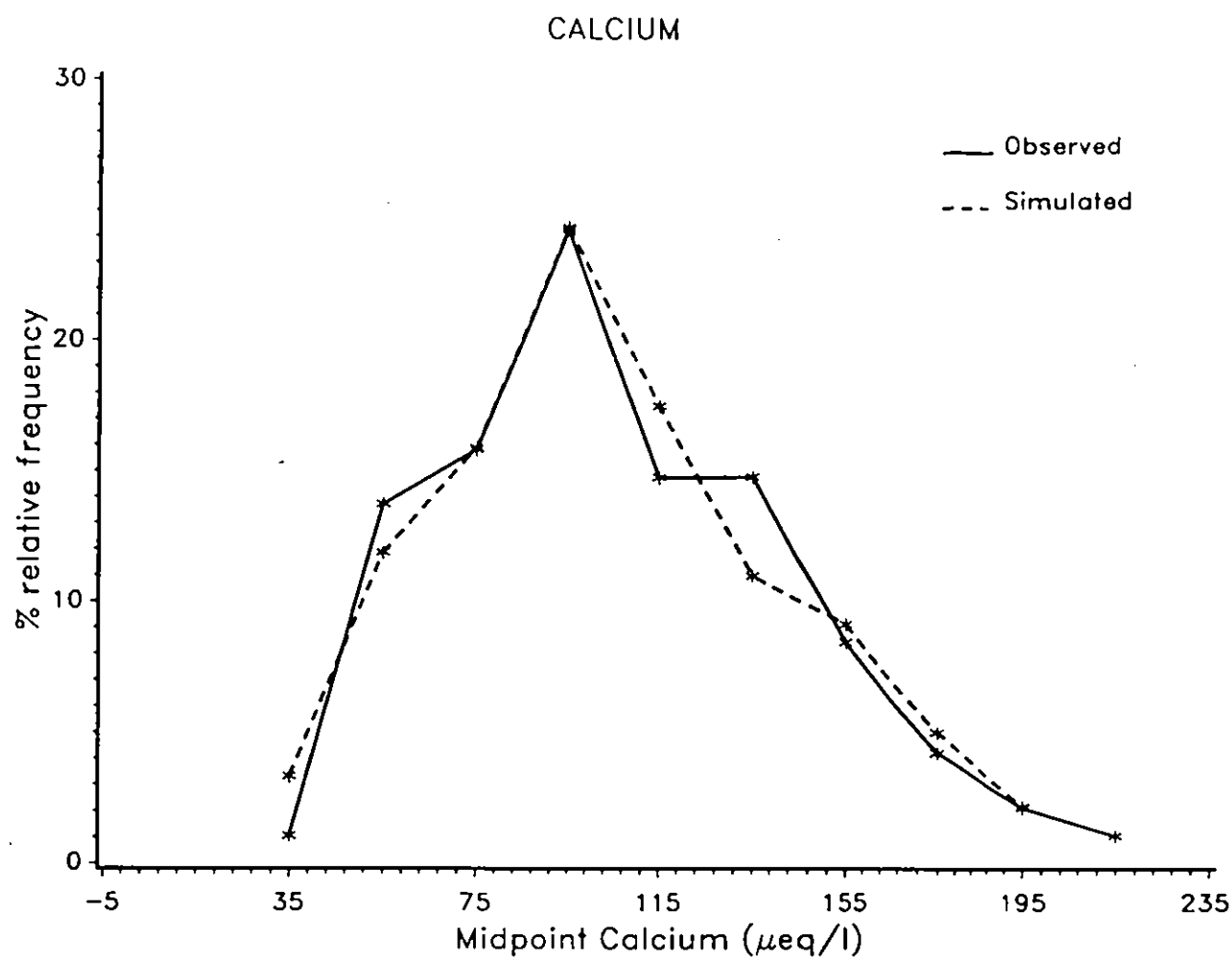


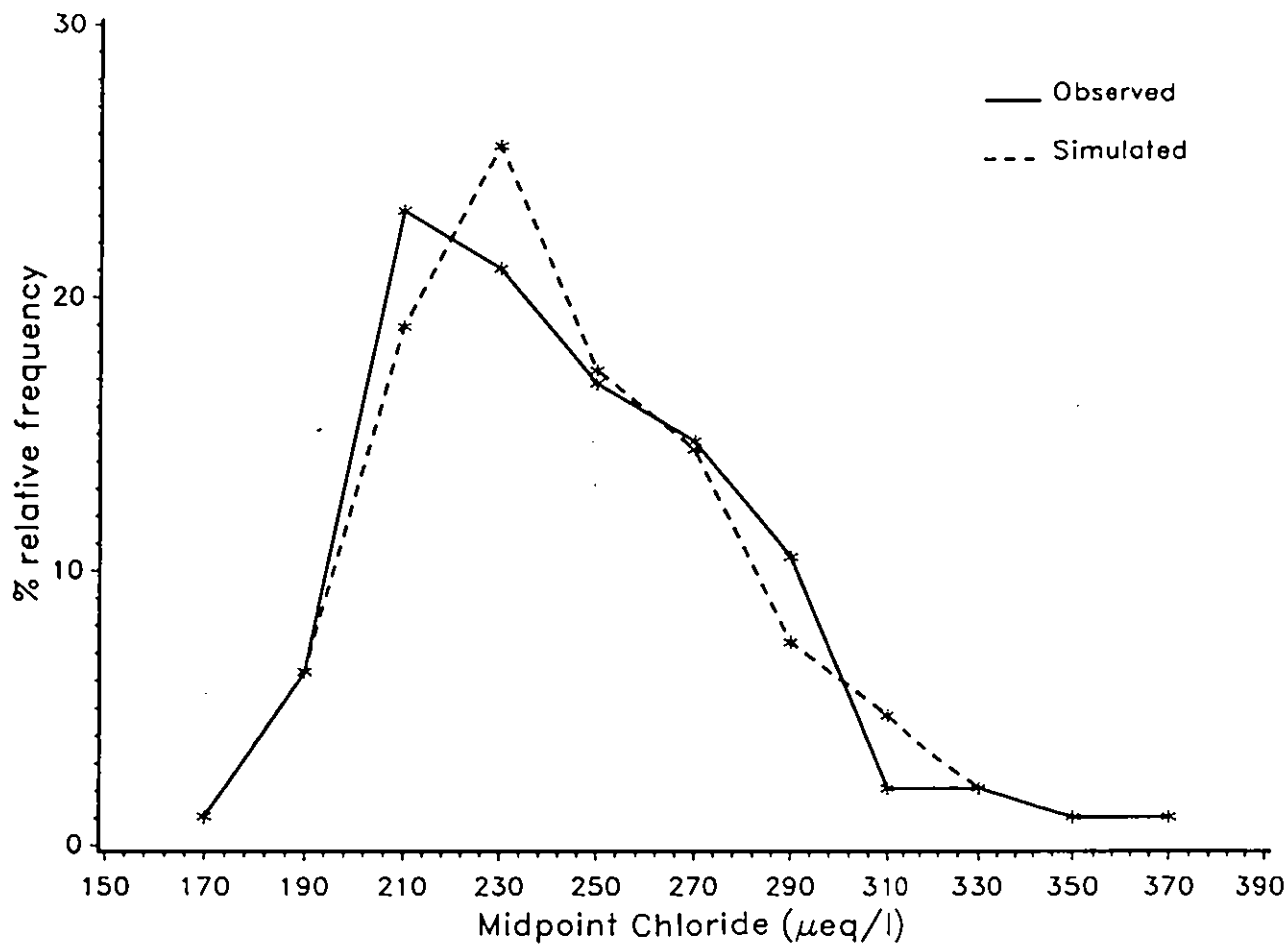
Figure 1 (d)





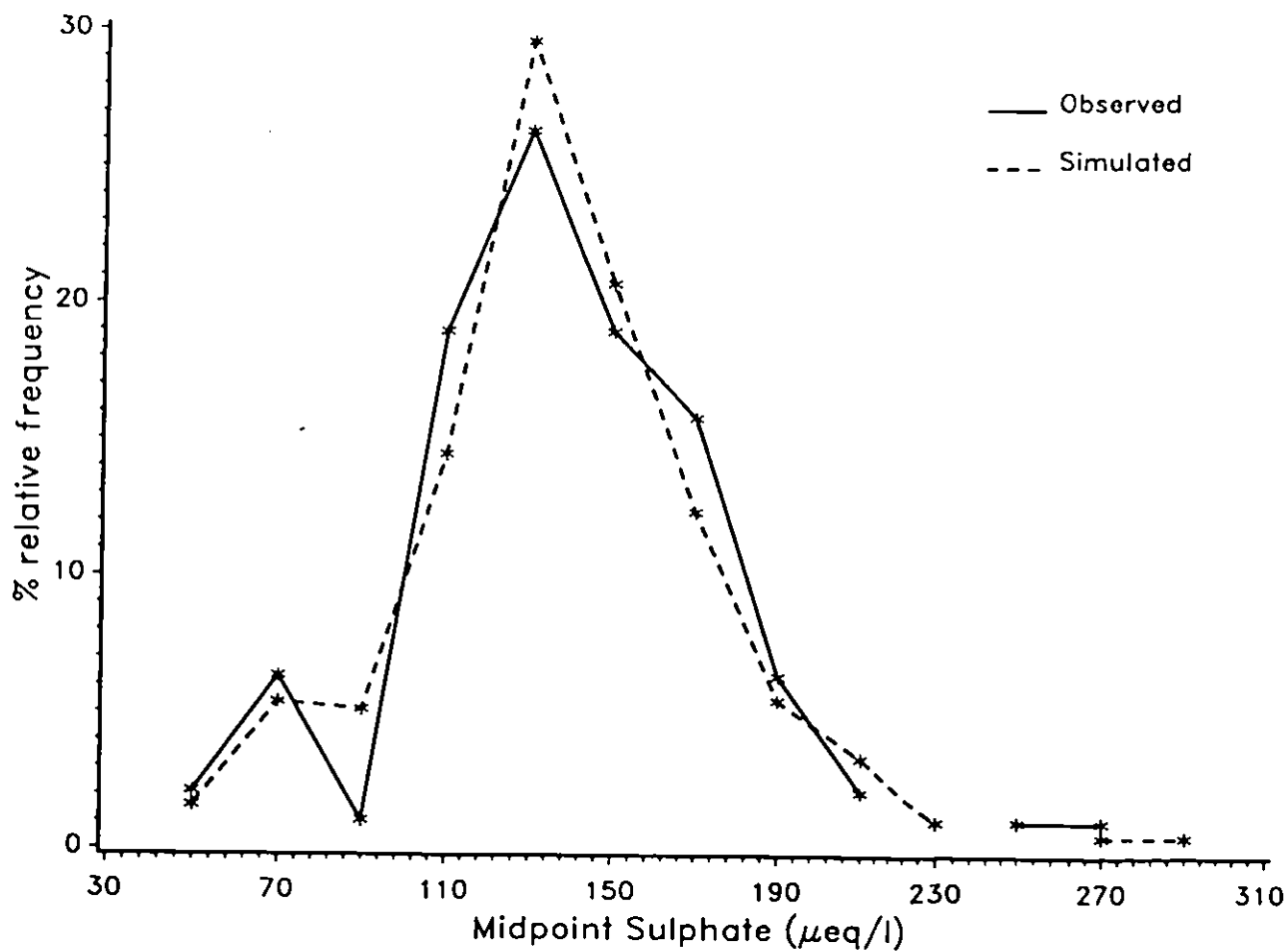
CHLORIDE

Figure 1 (g)



SULPHATE

Figure 1 (h)



NITRATE

Figure 1 (i)

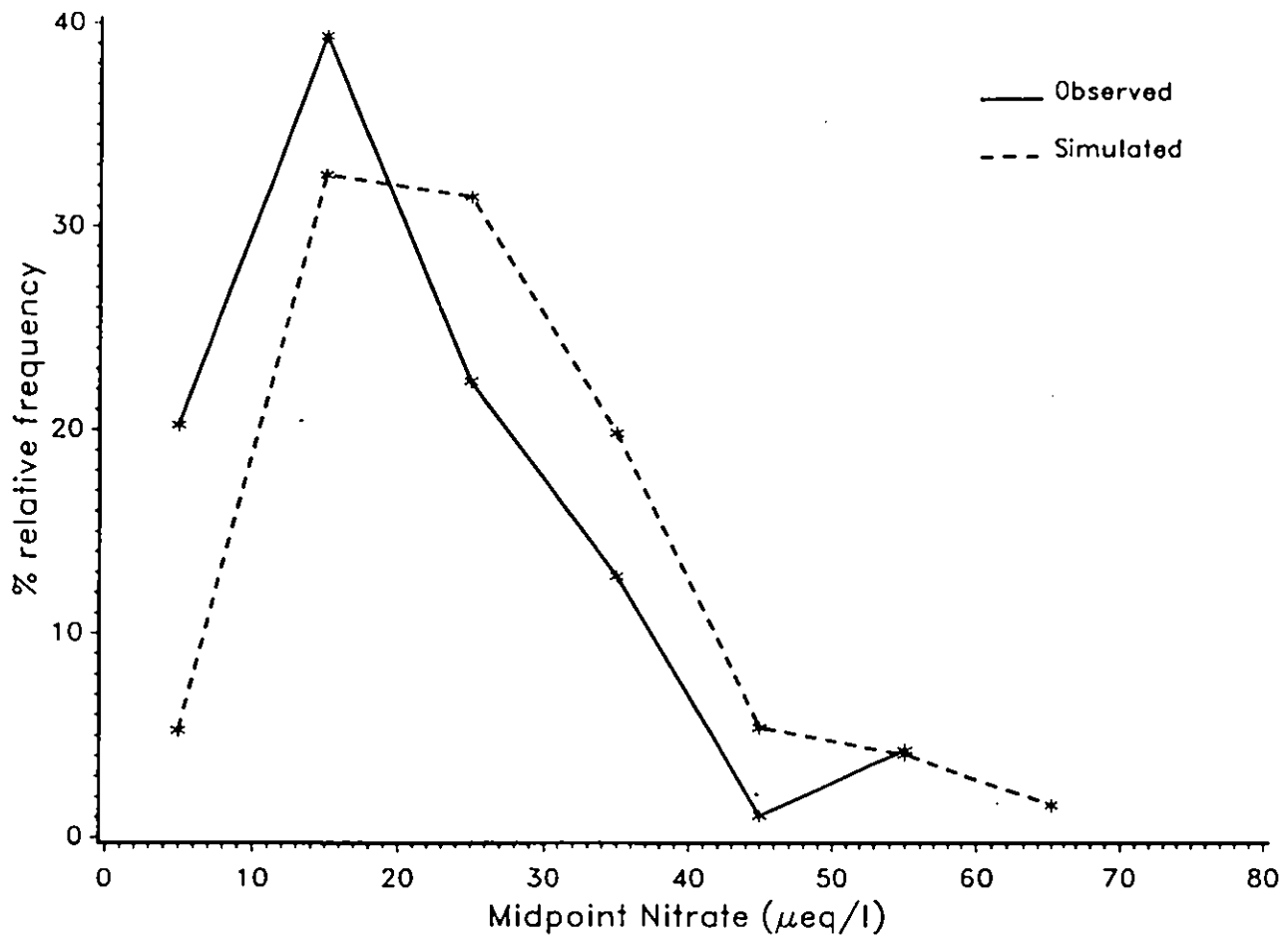


Figure 2

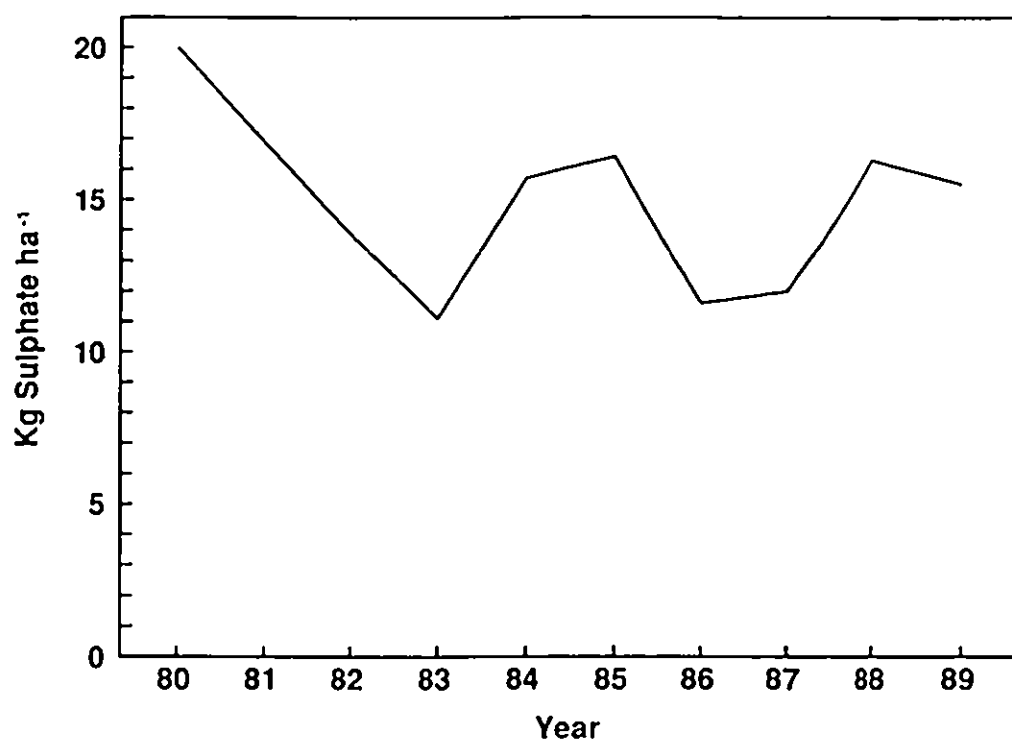


Figure 3

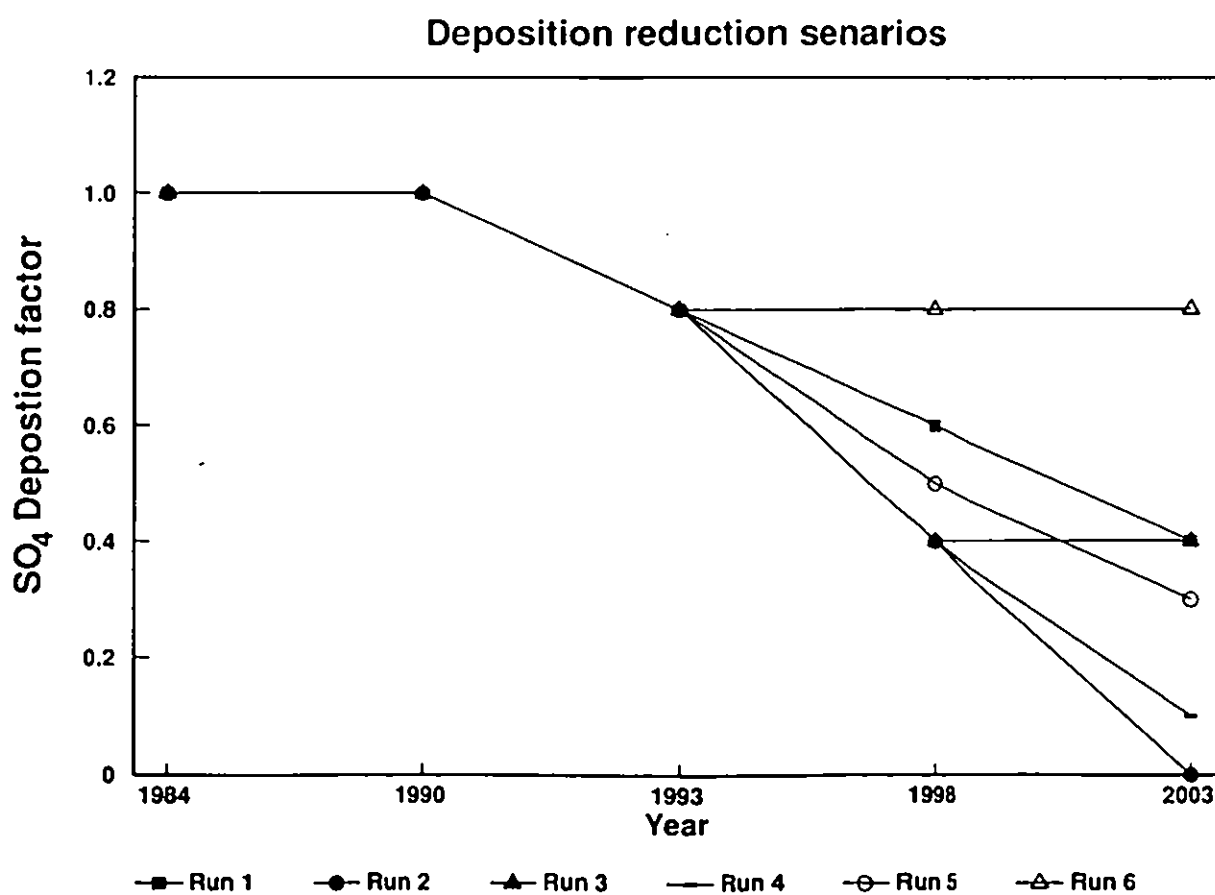


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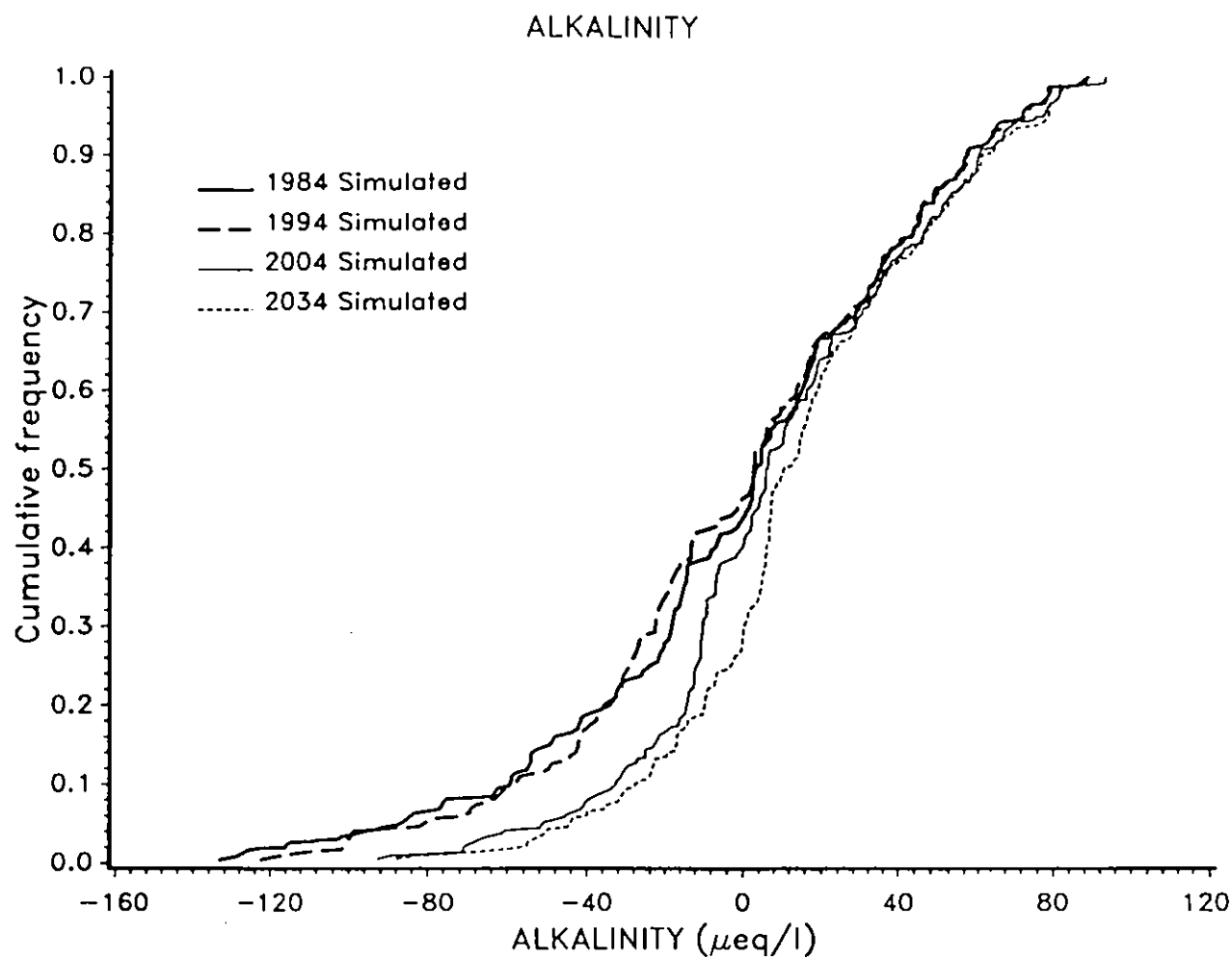


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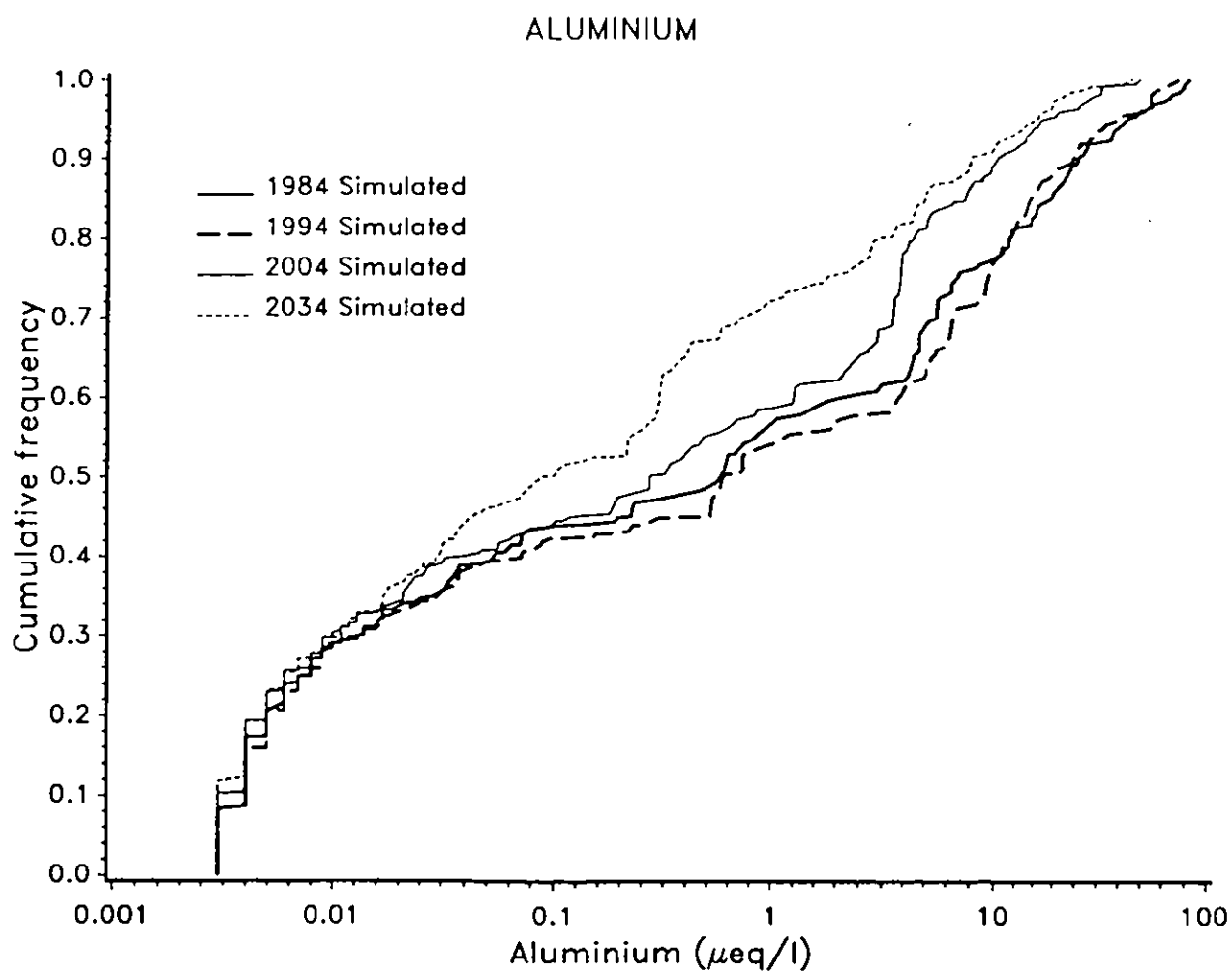


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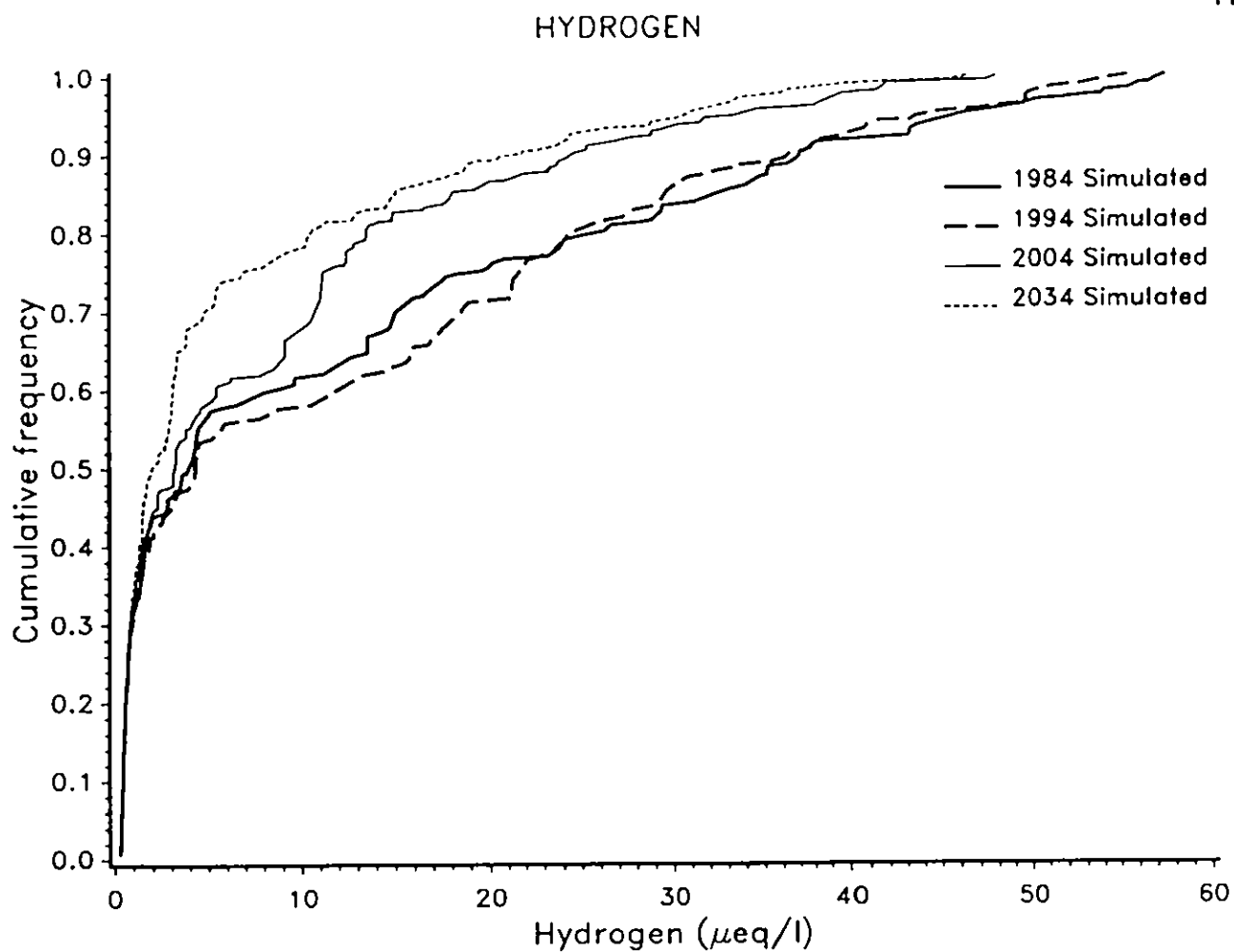


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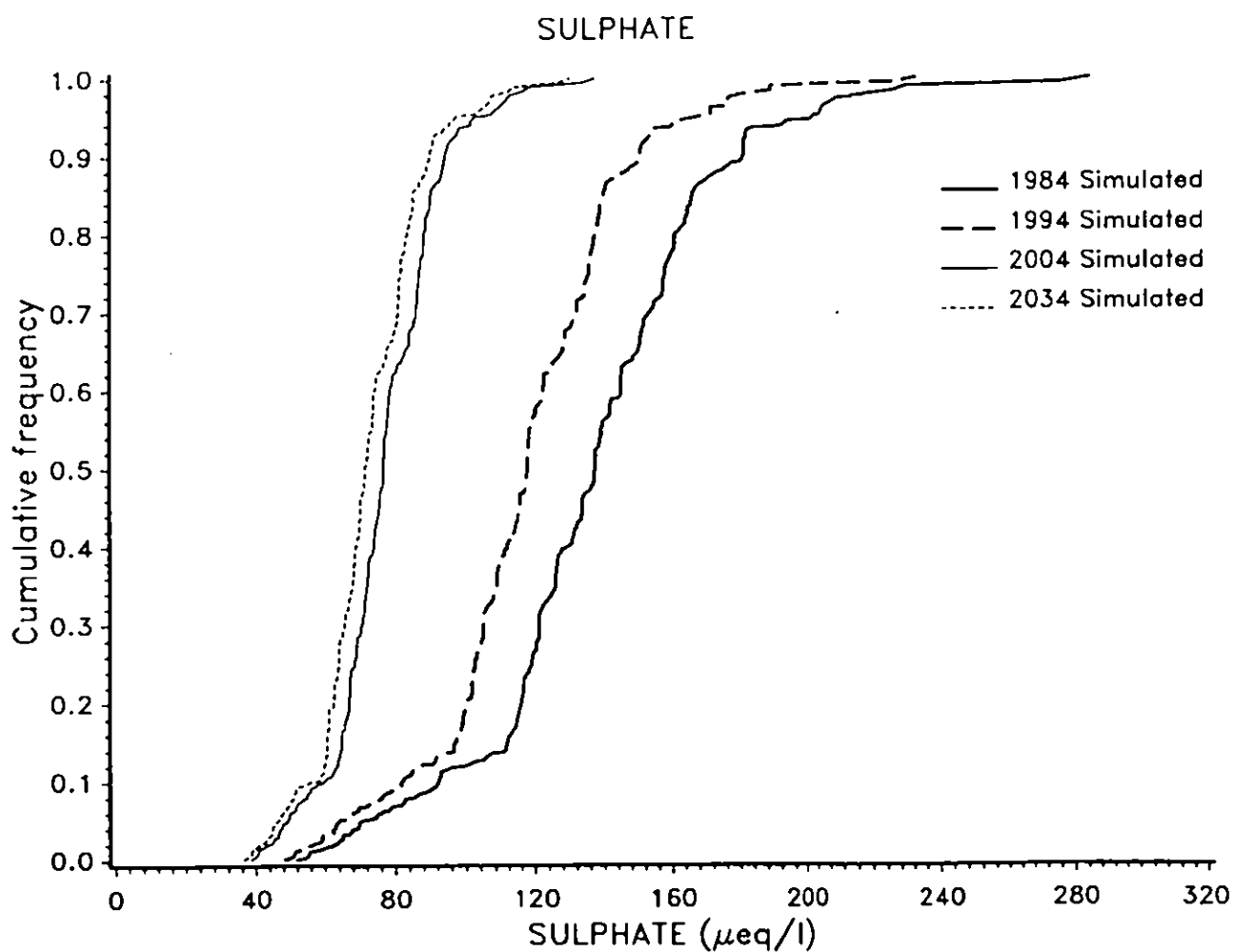


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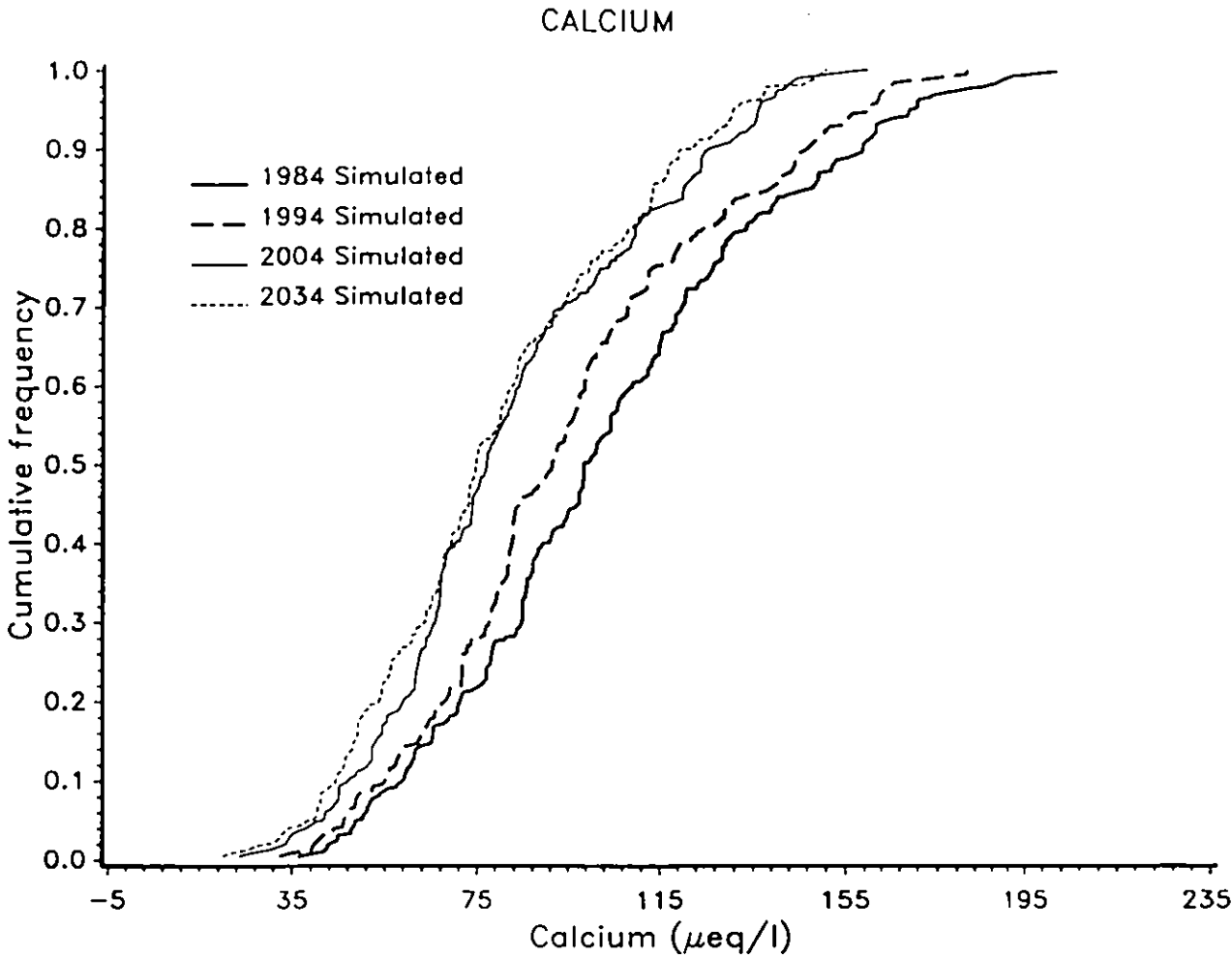
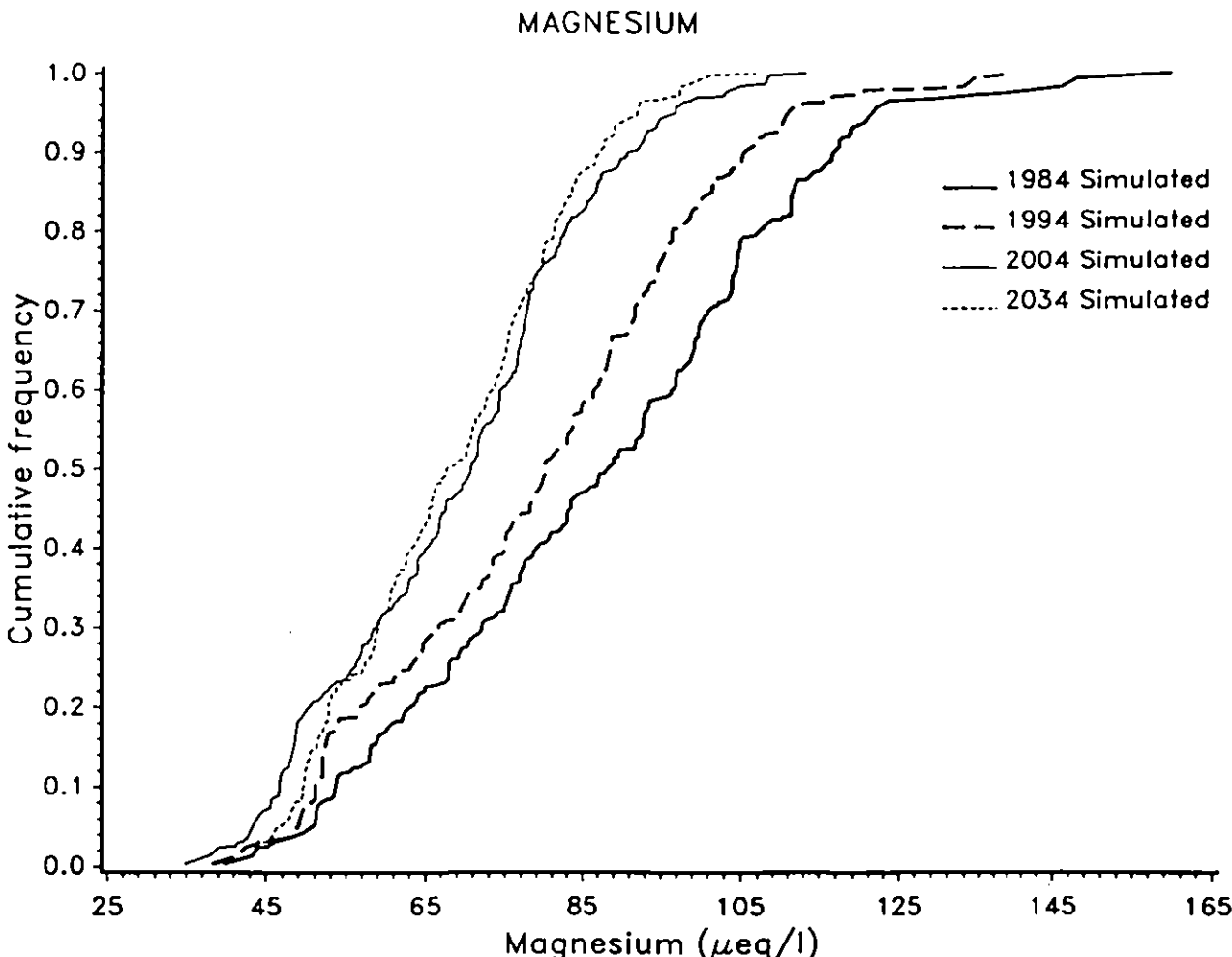


Figure 4 (f)



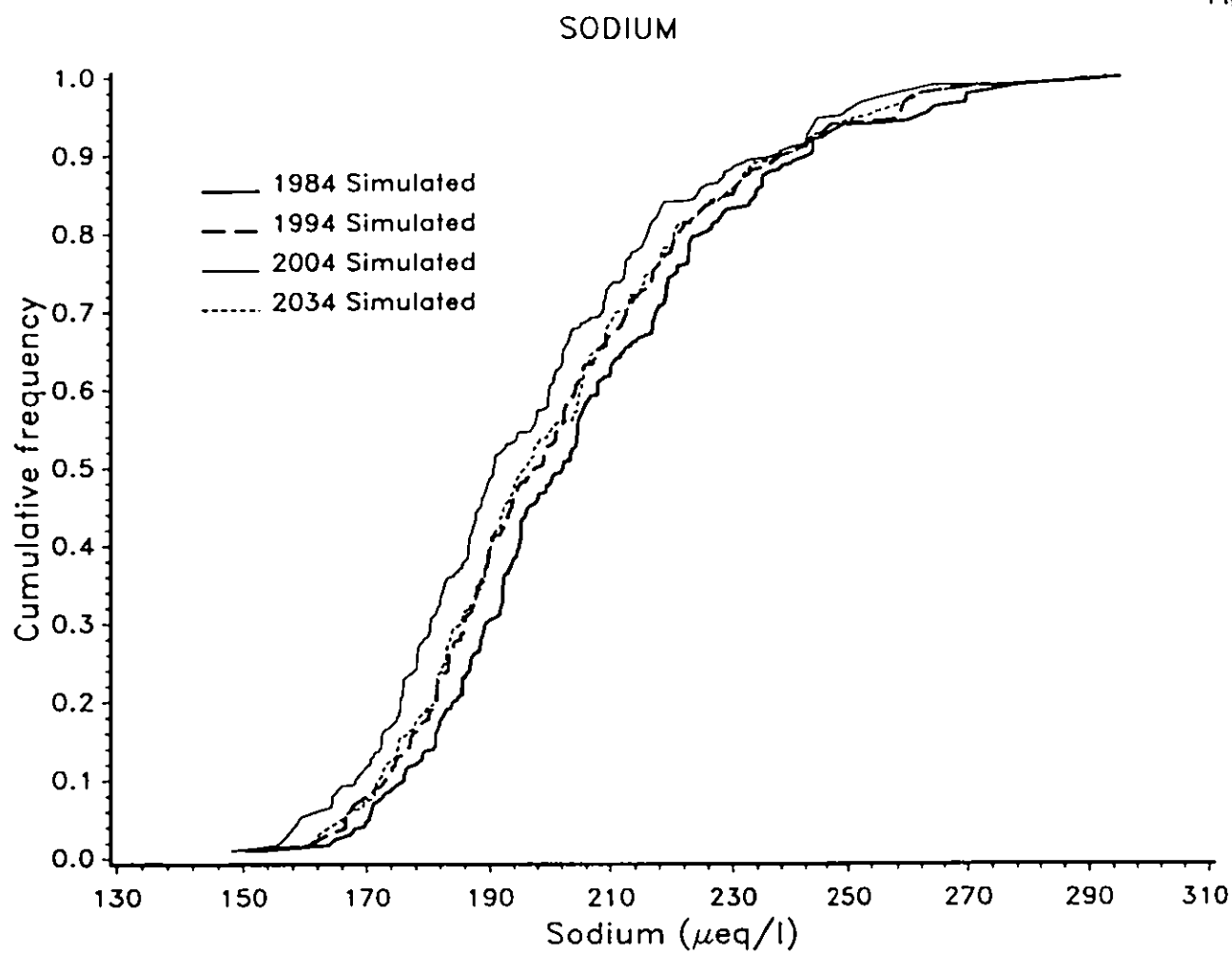


Figure 5 (a)

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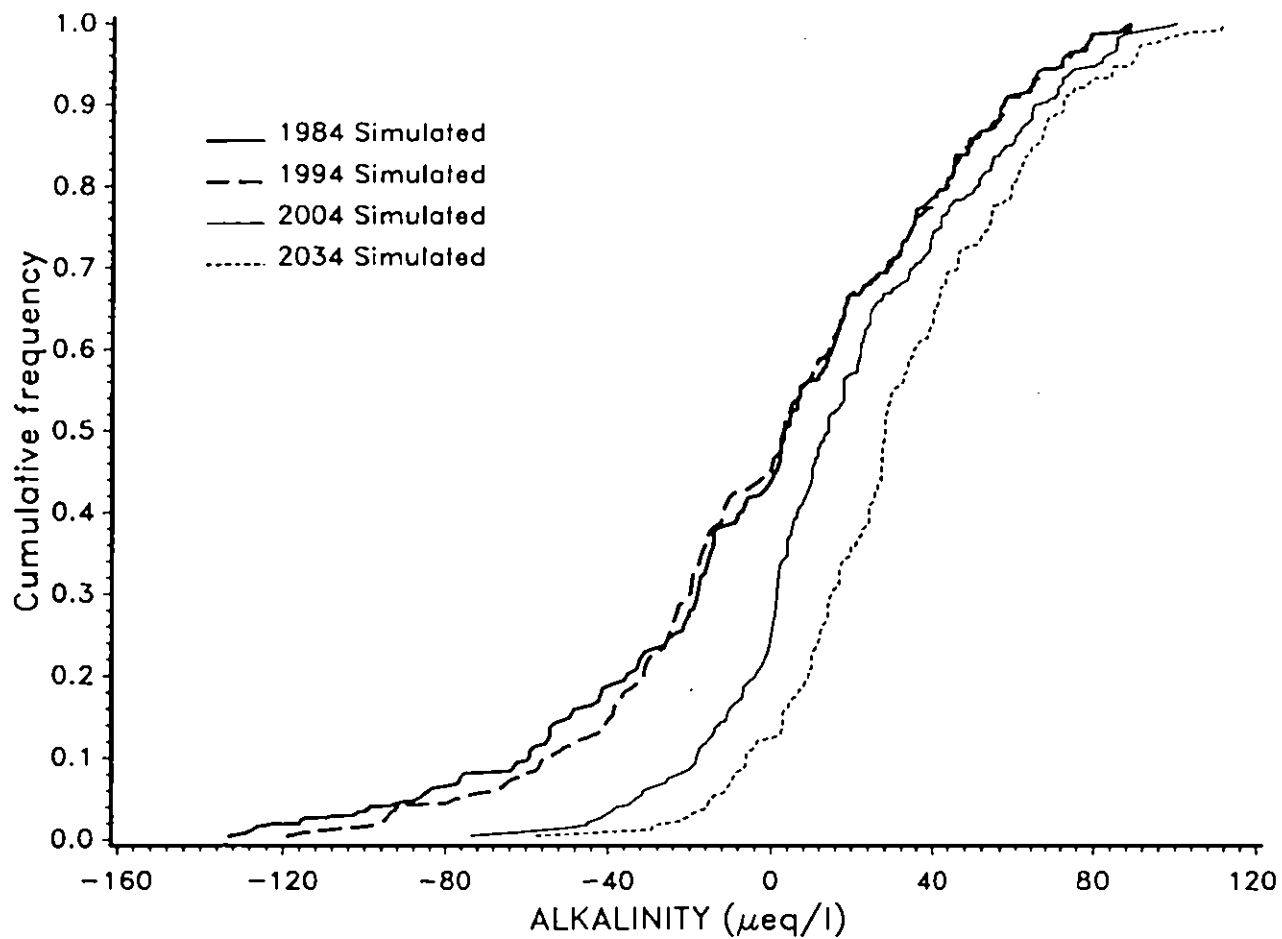


Figure 5 (b)

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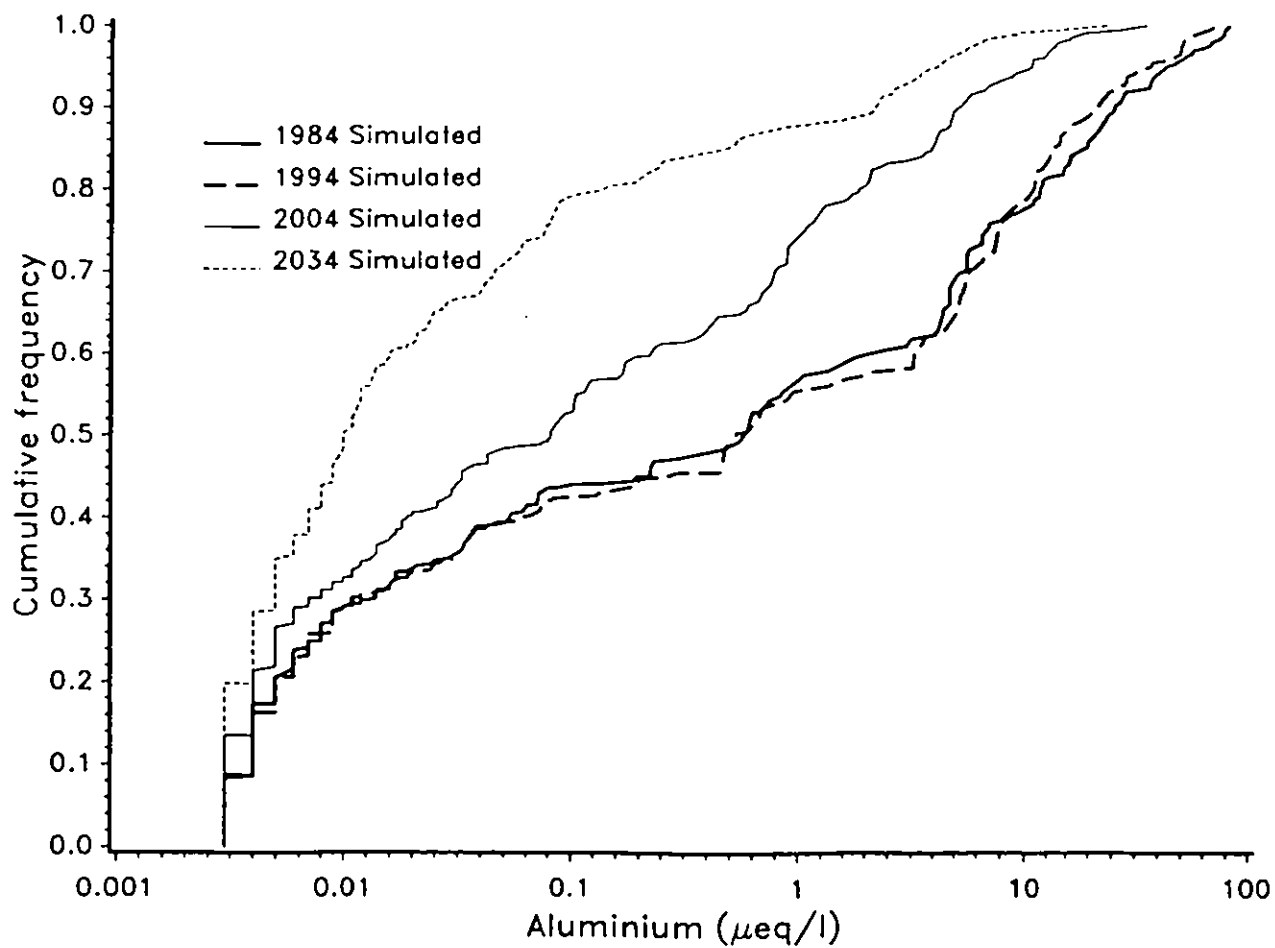


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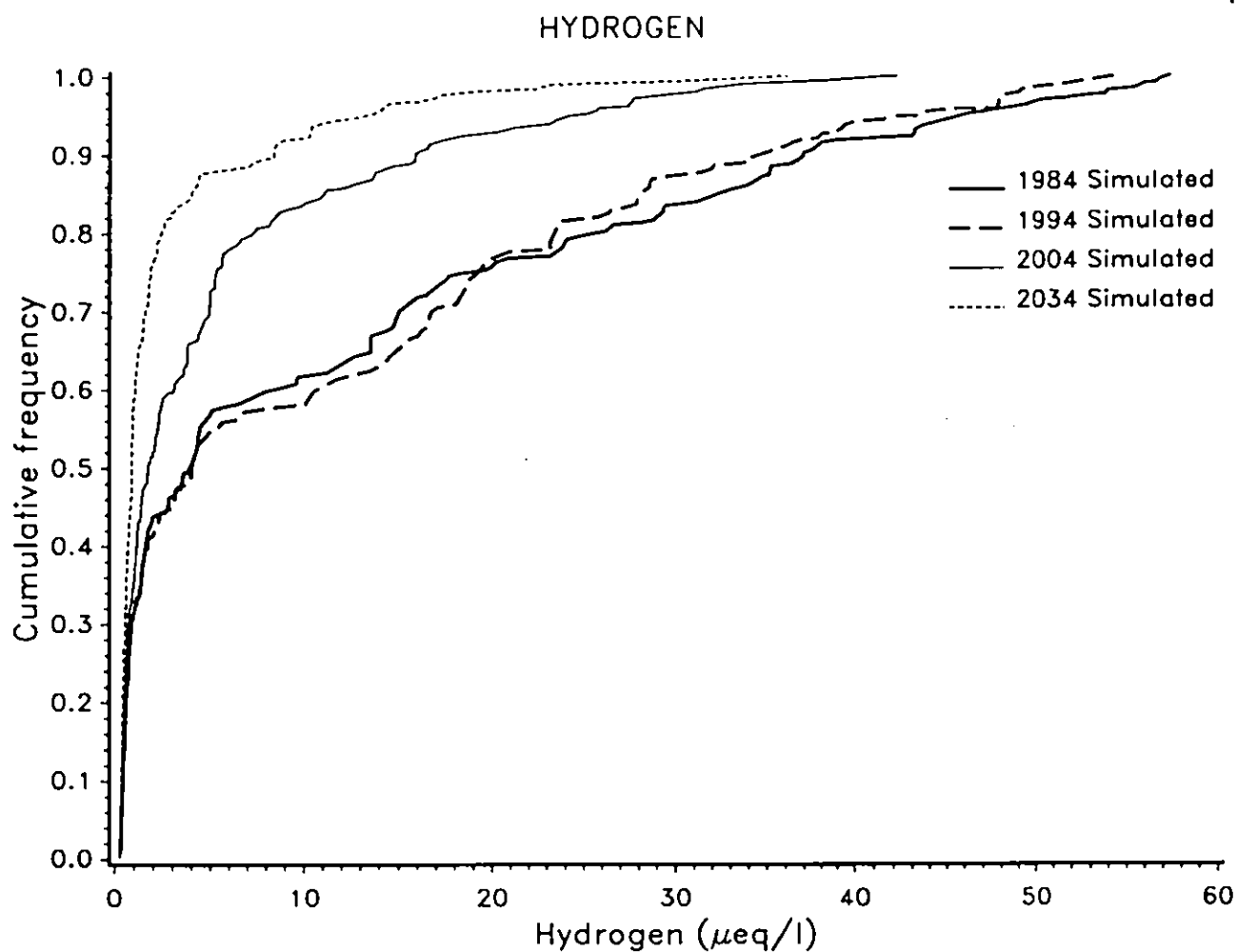


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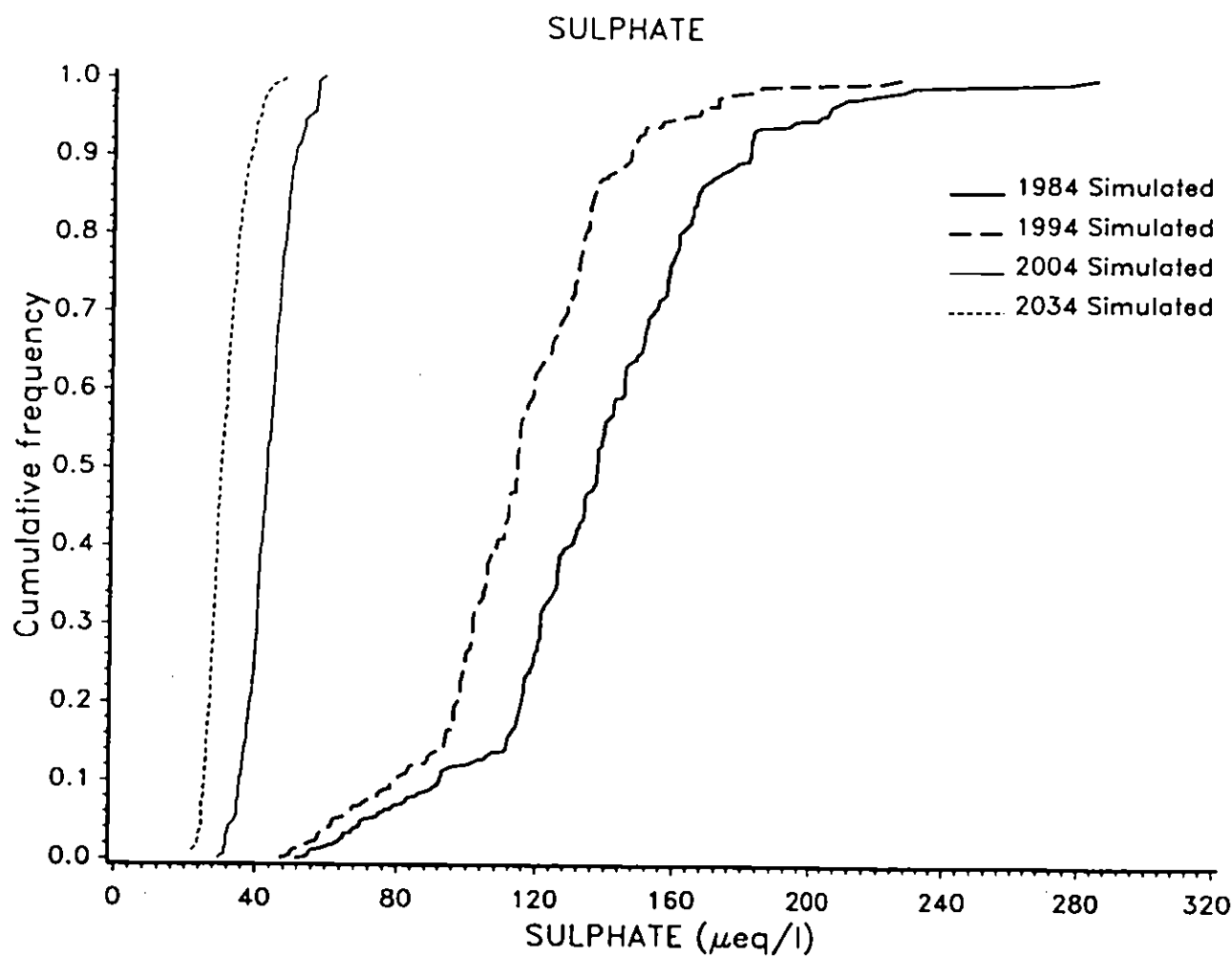


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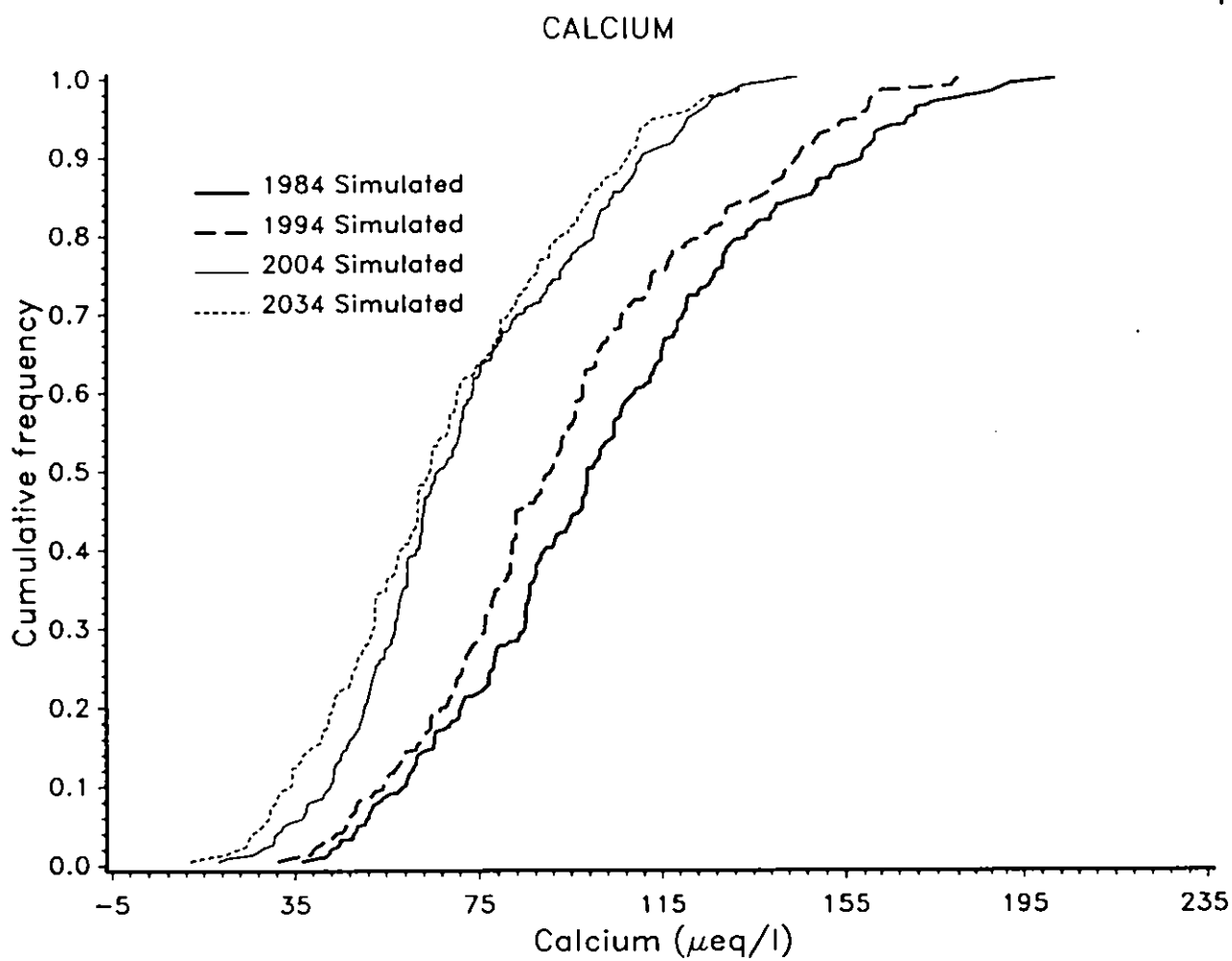
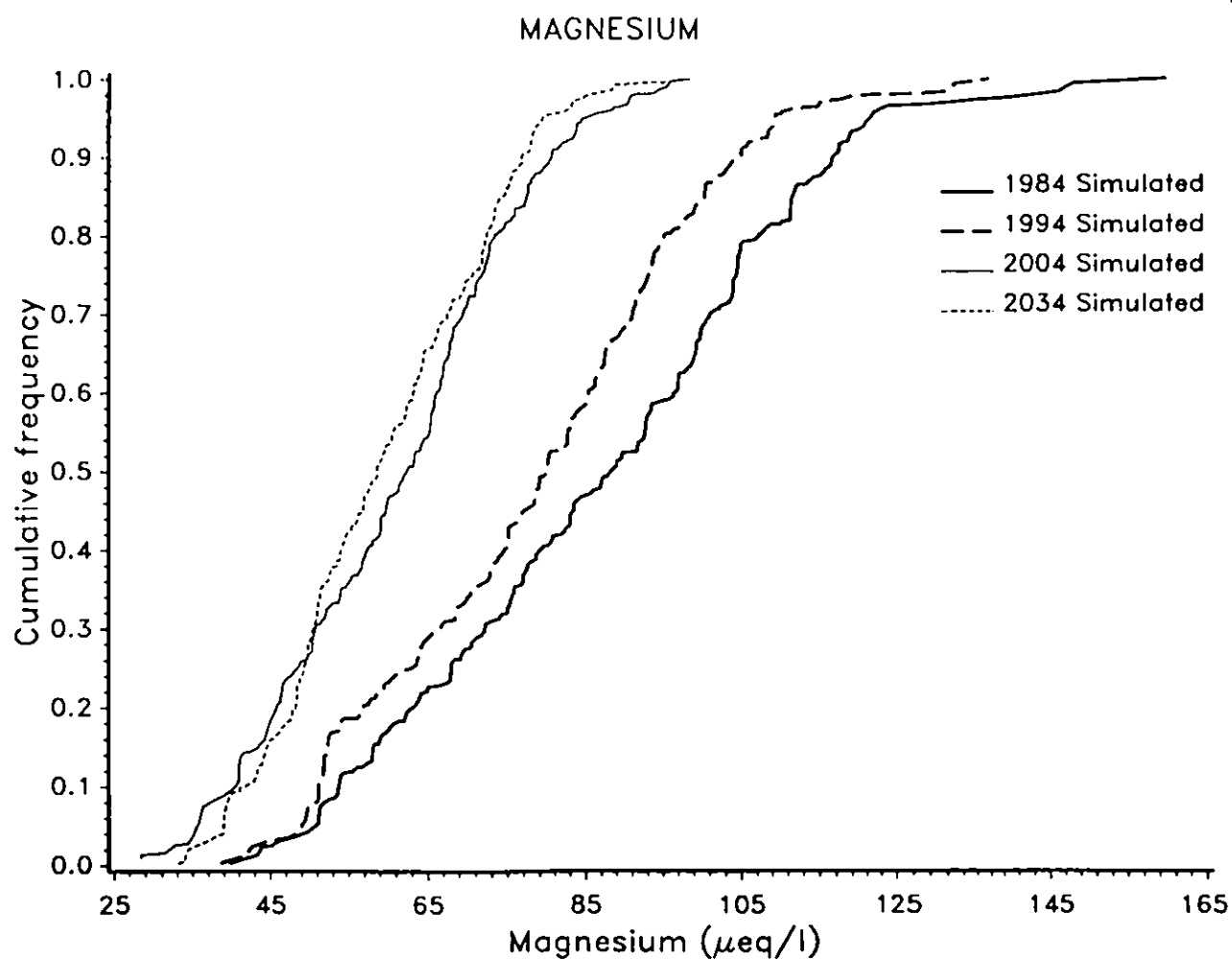


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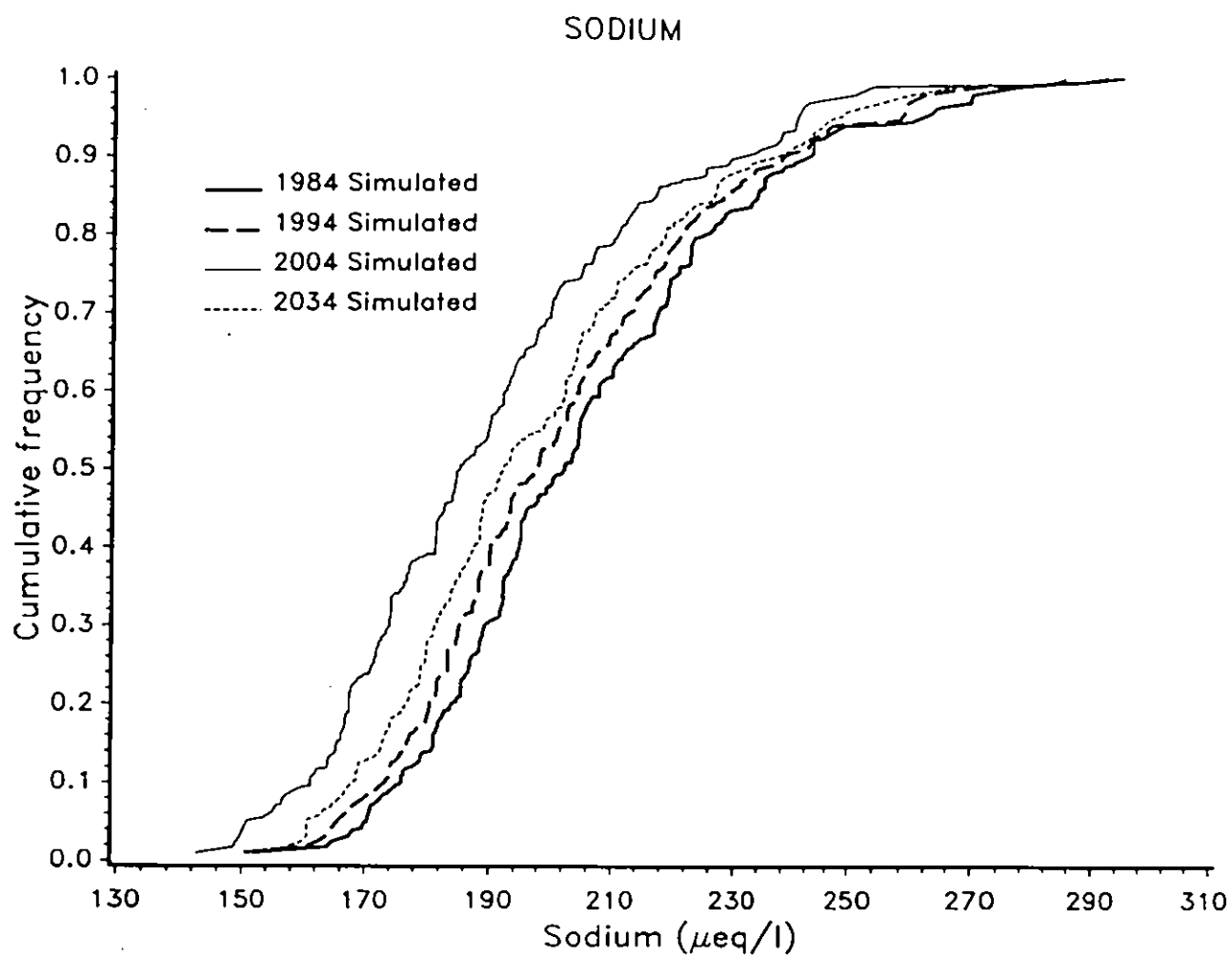


Figure 6 (a)

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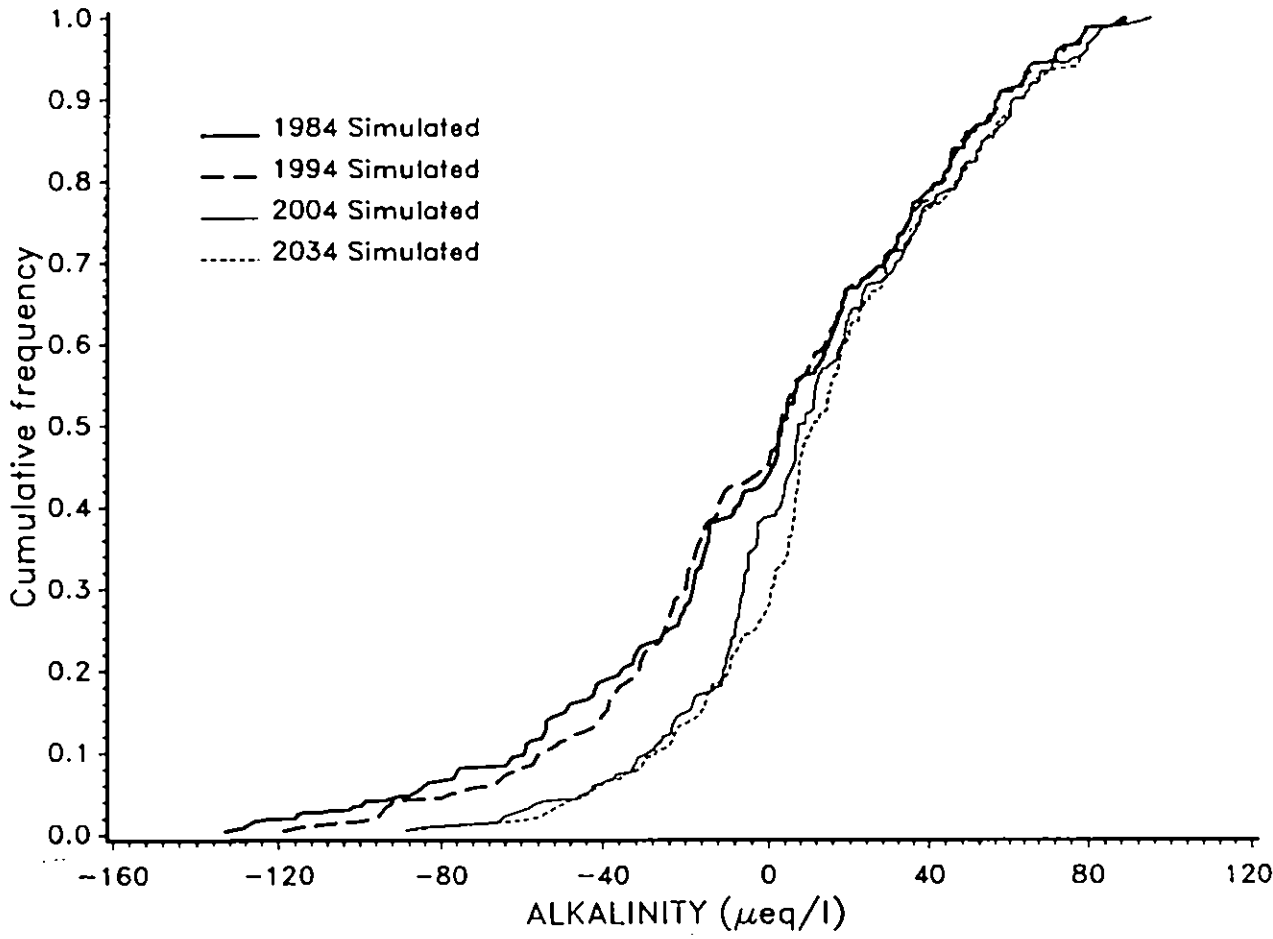


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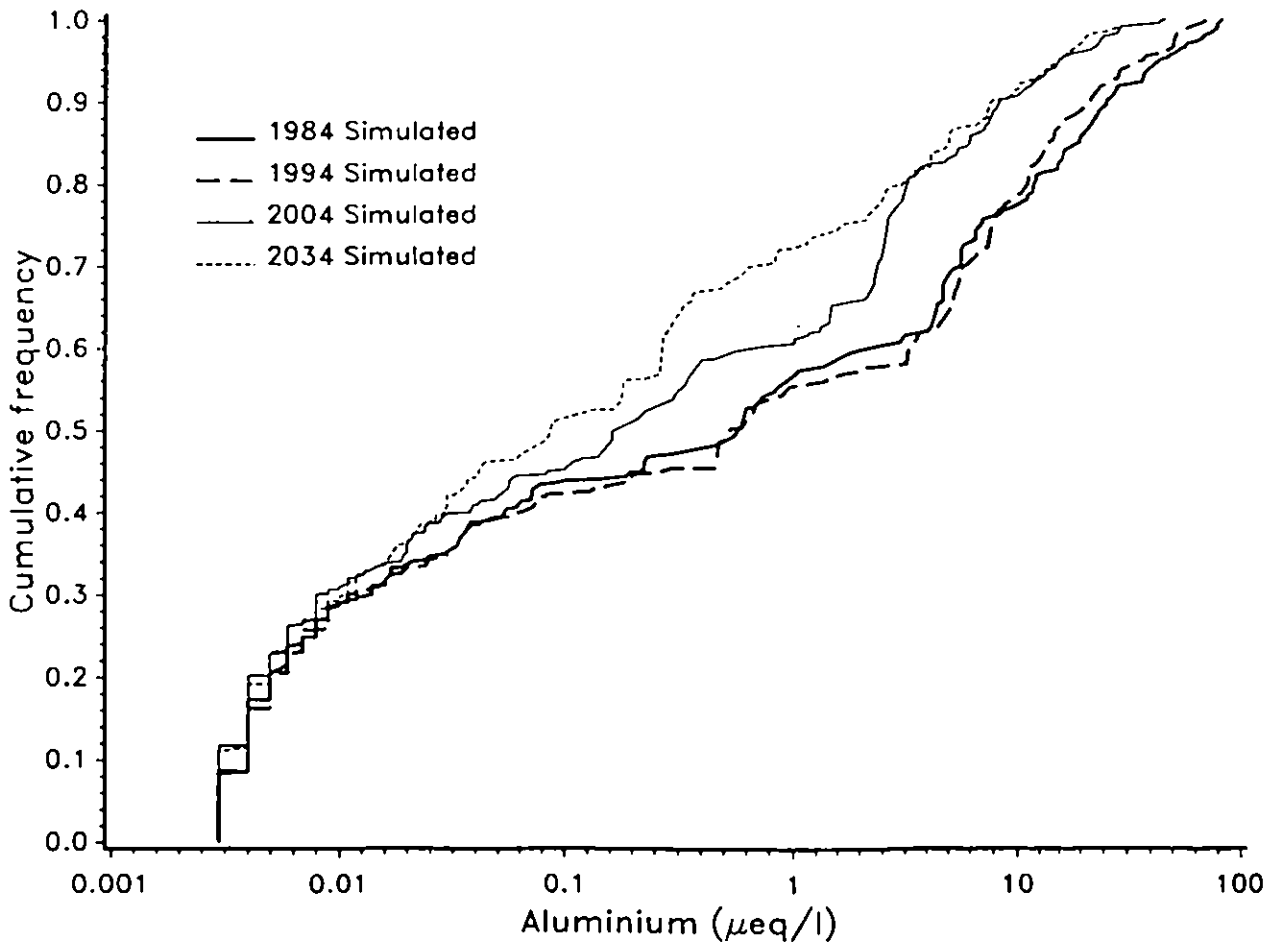


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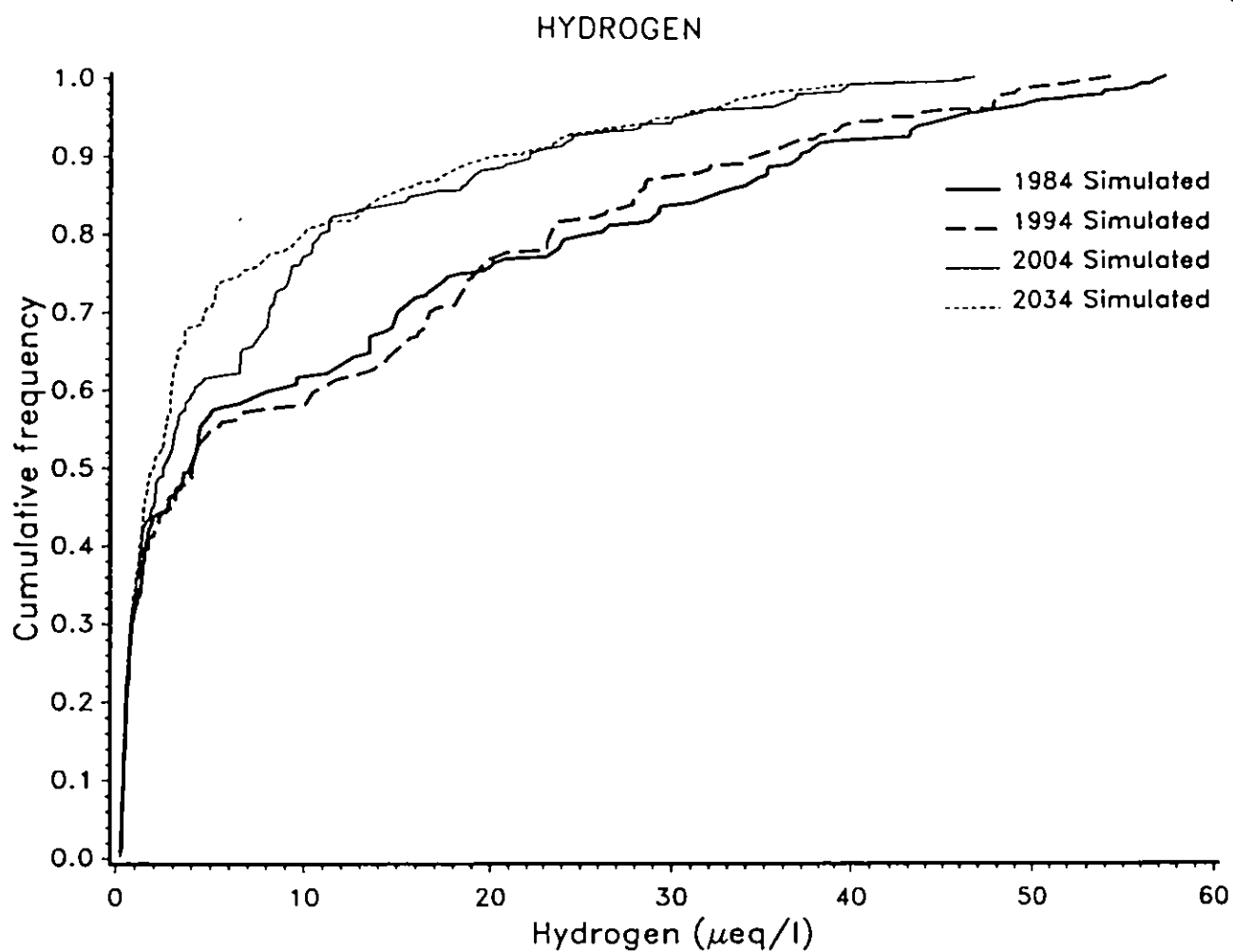


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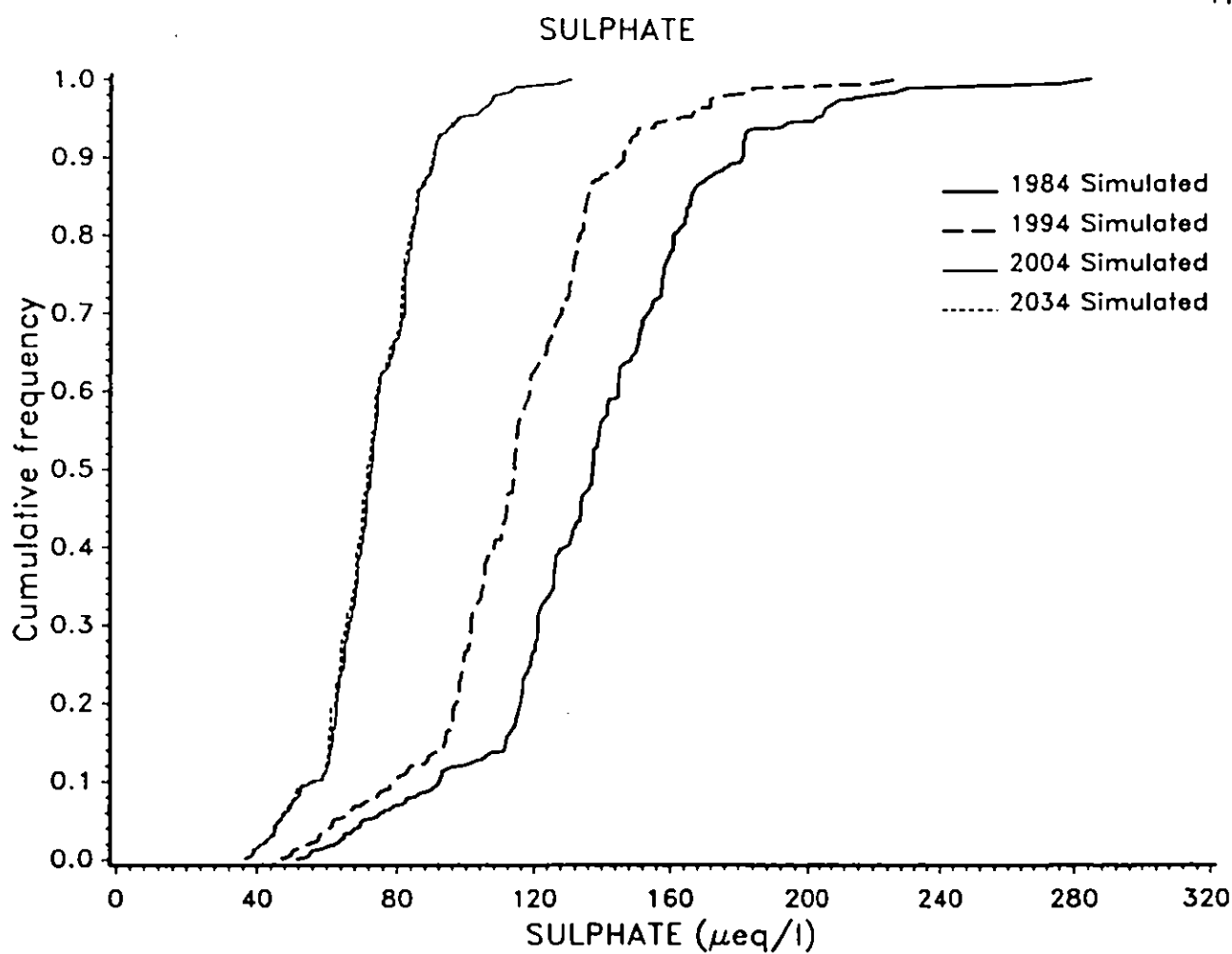


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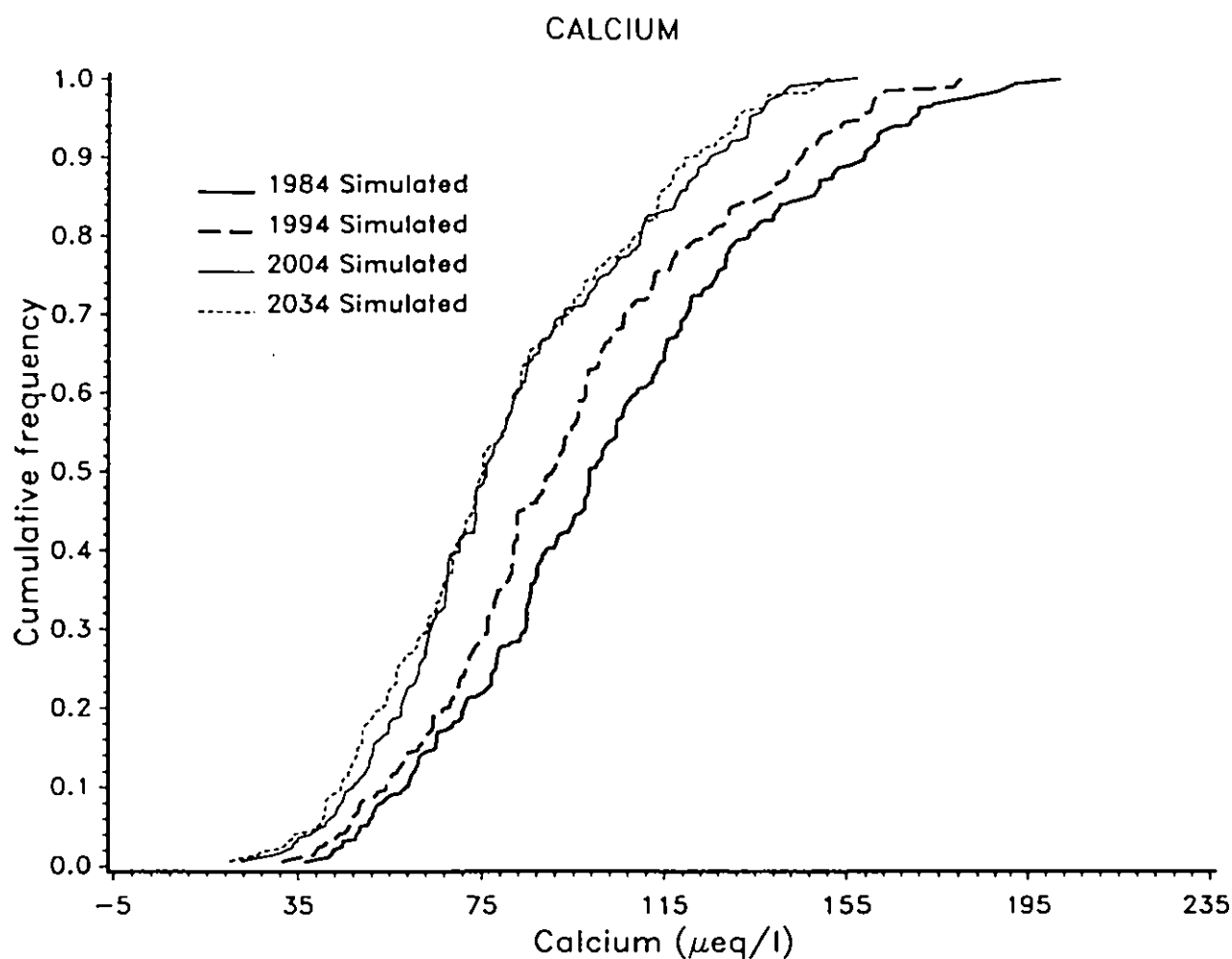
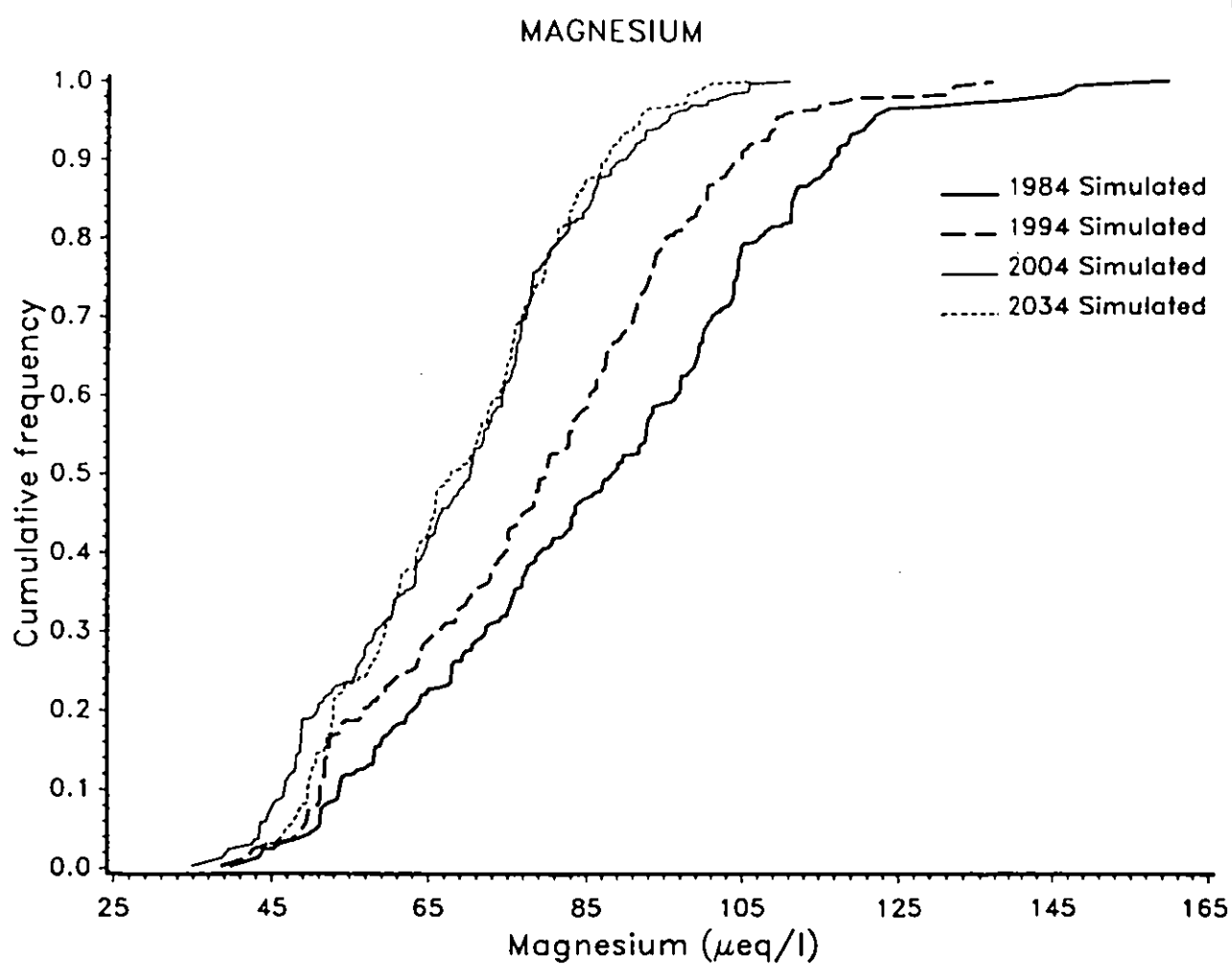


Figure 6 (f)



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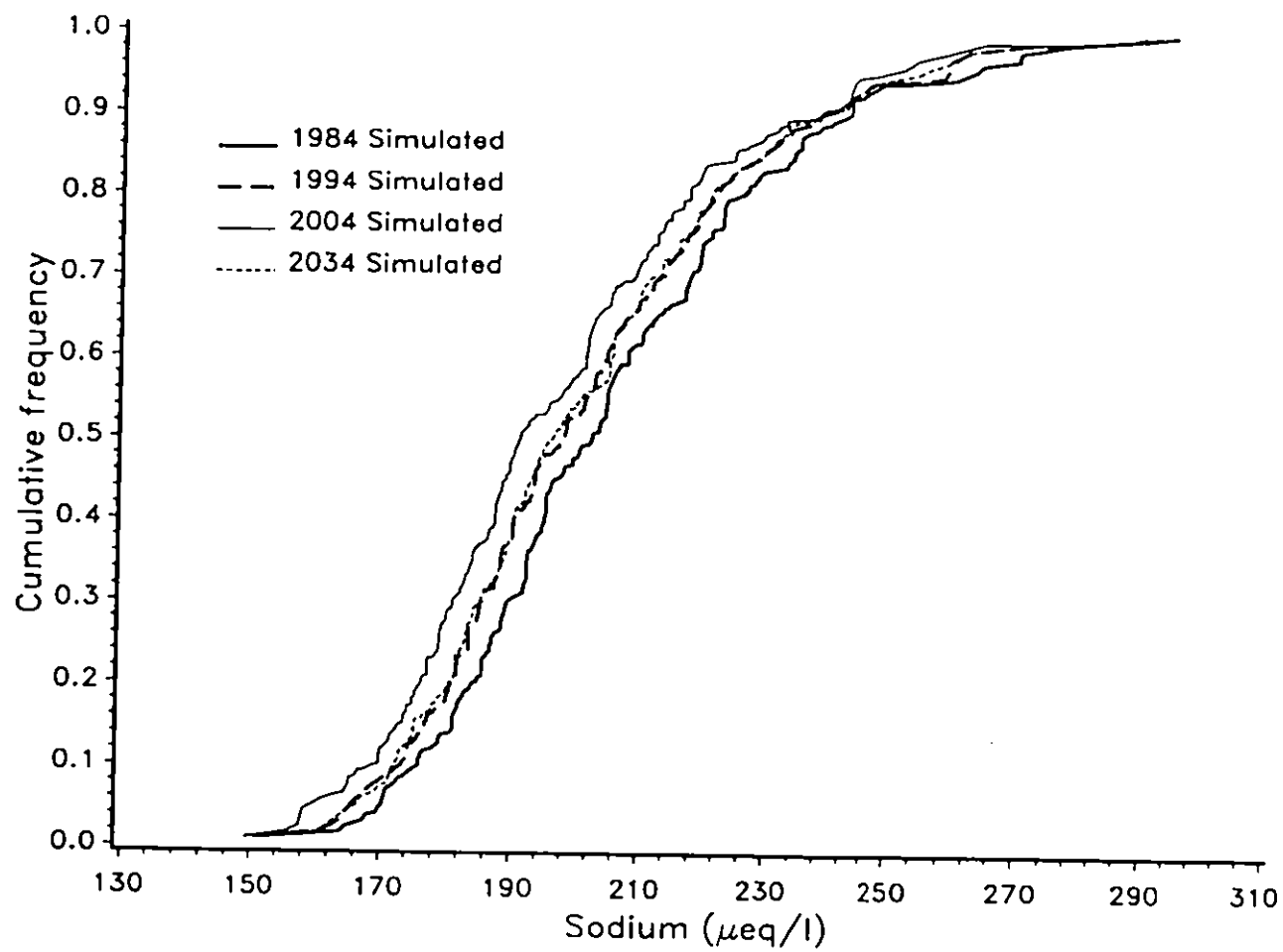


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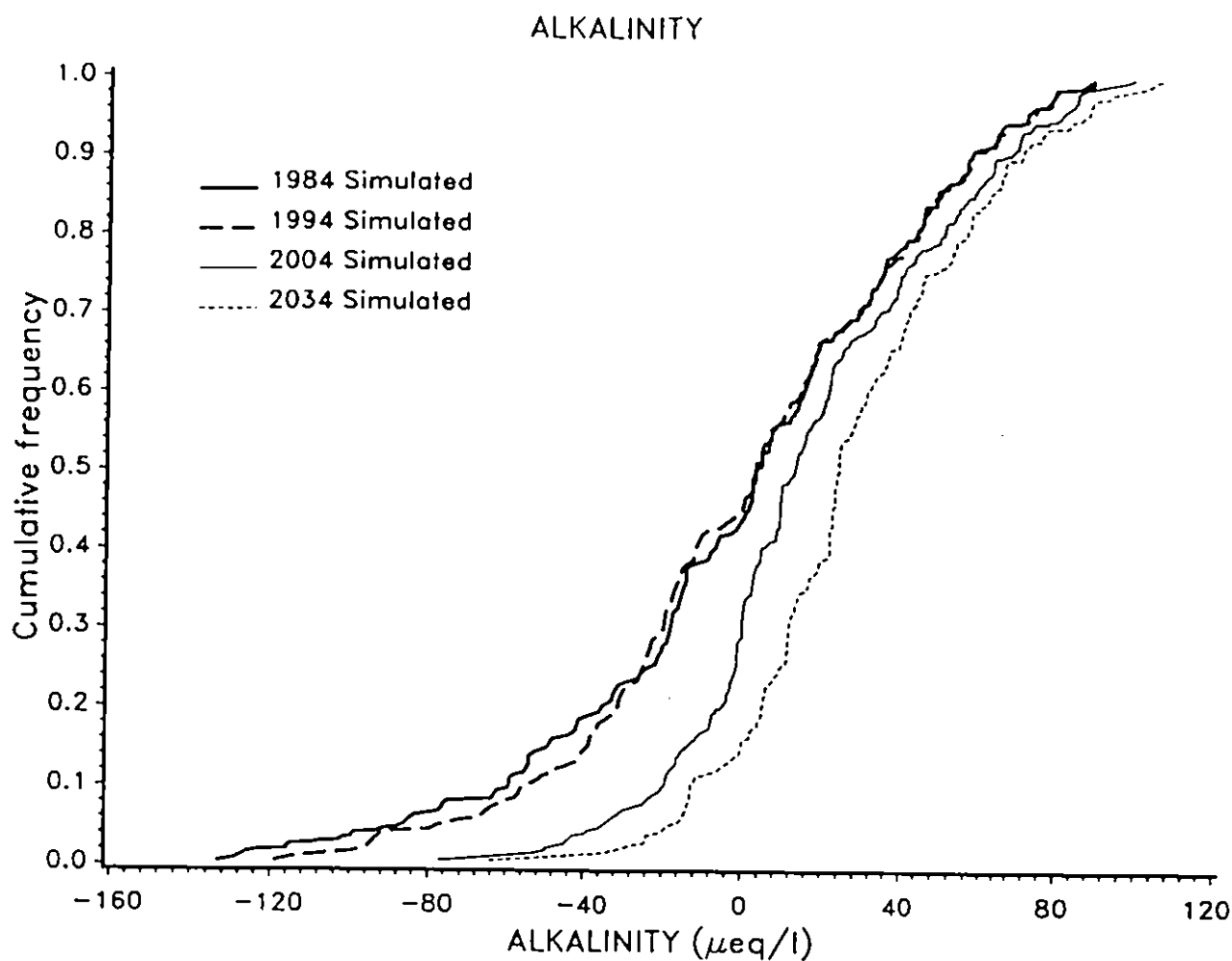


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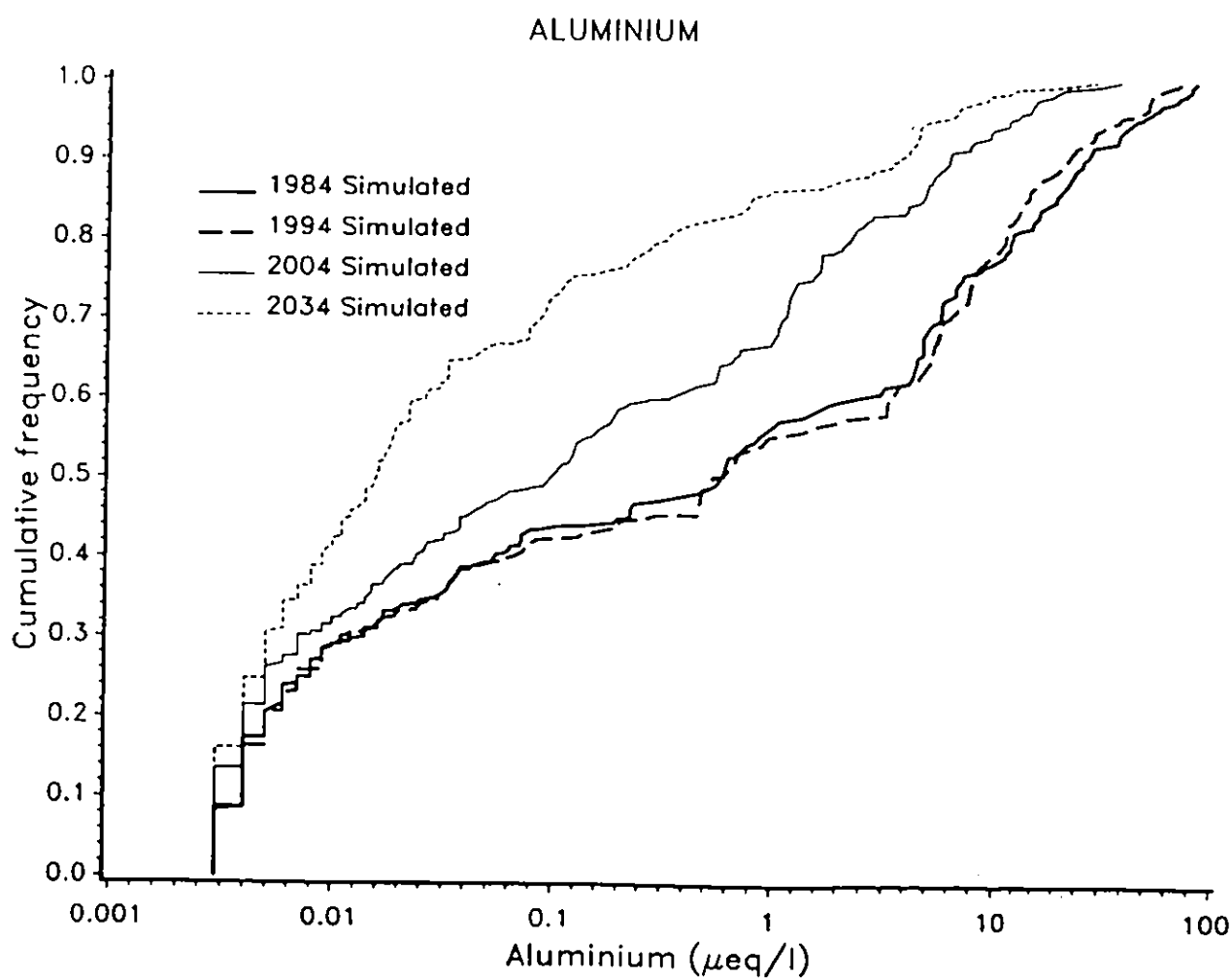


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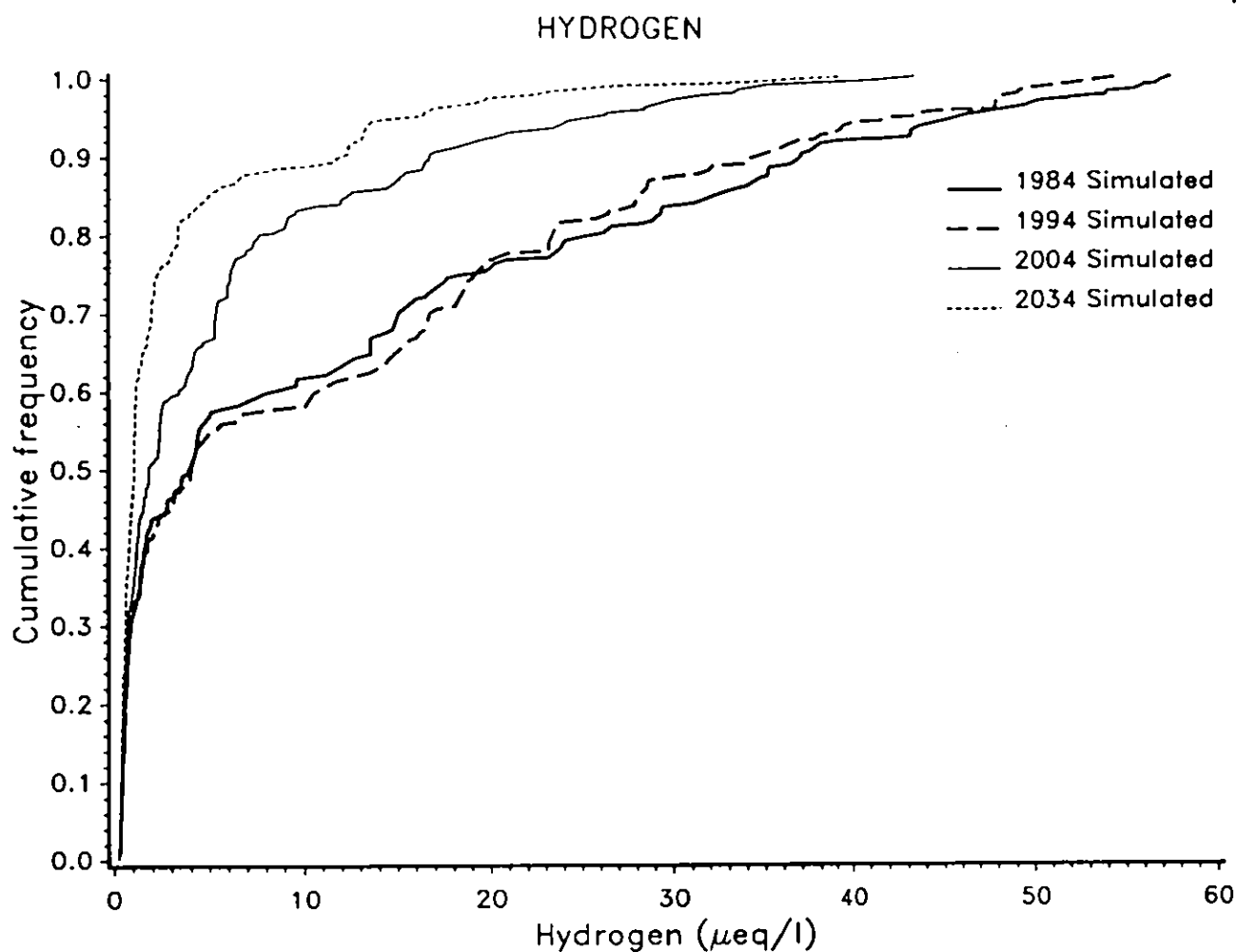


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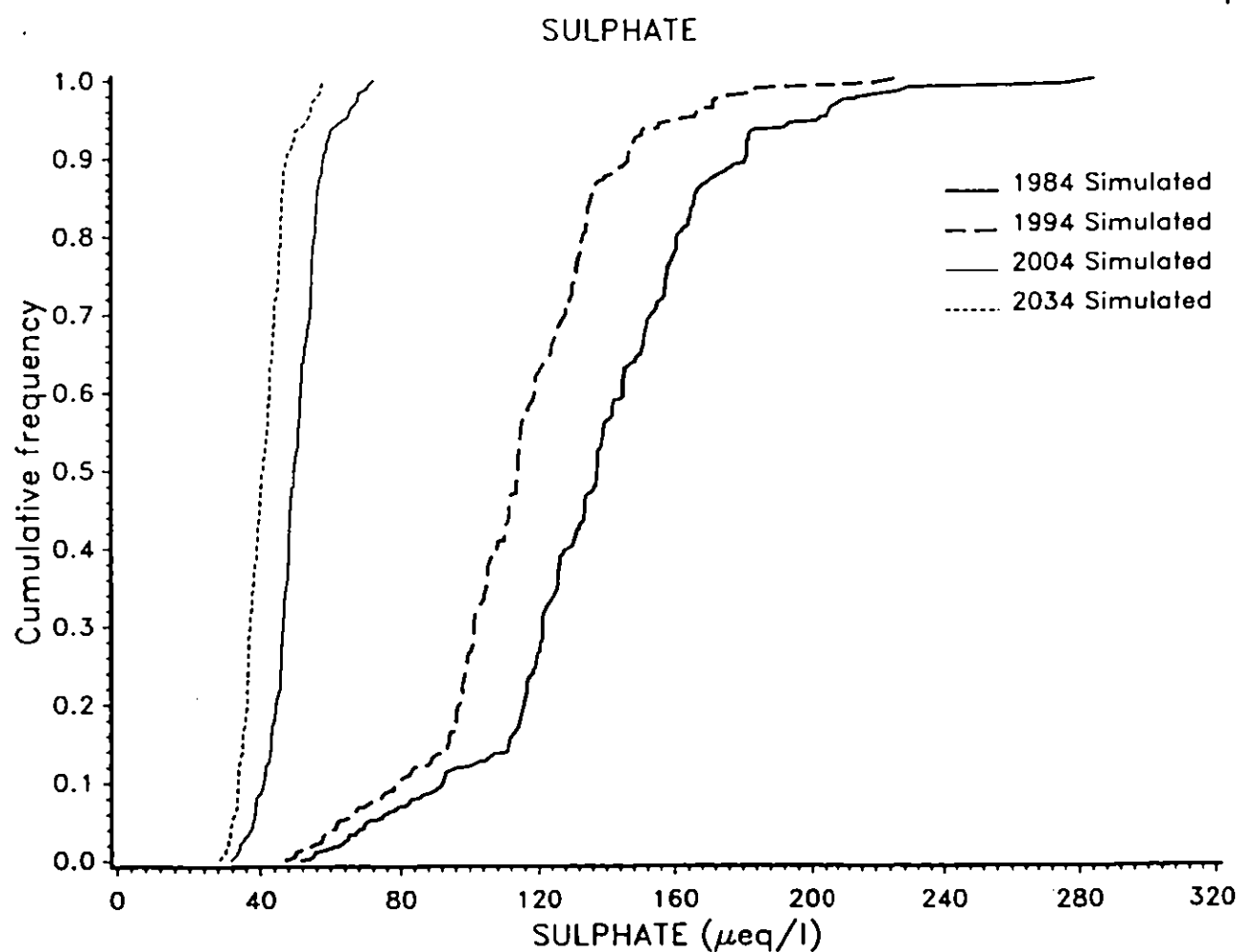


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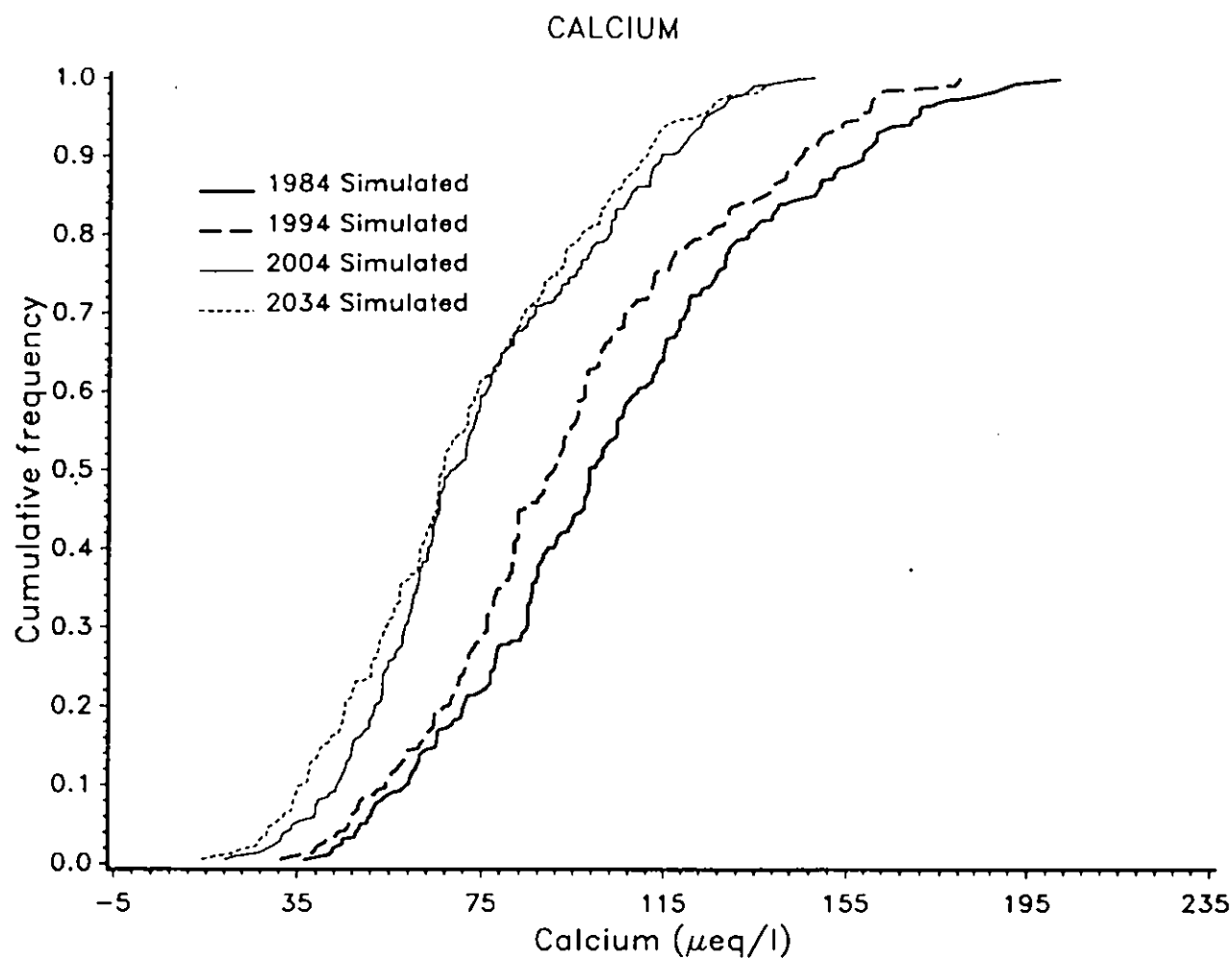
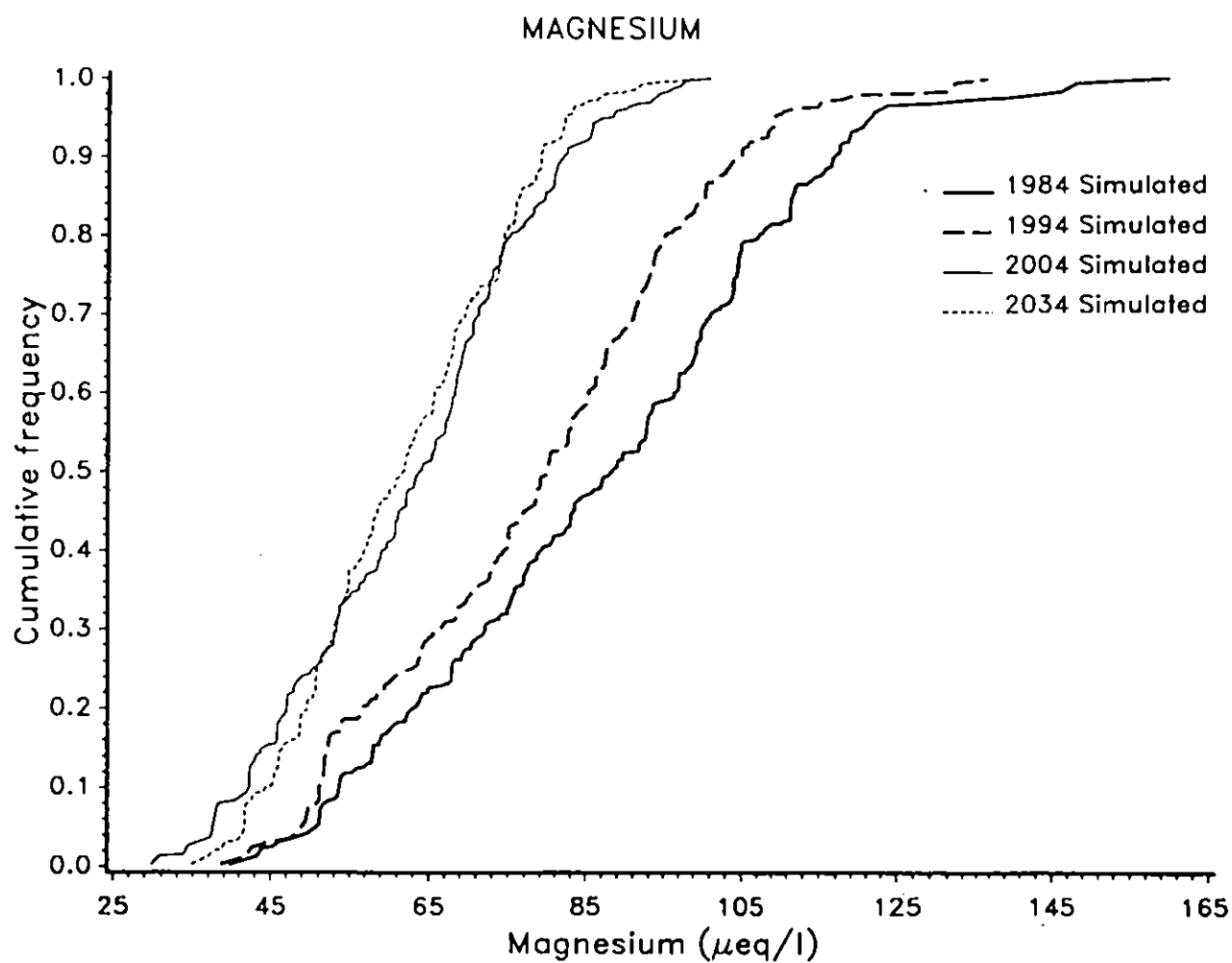


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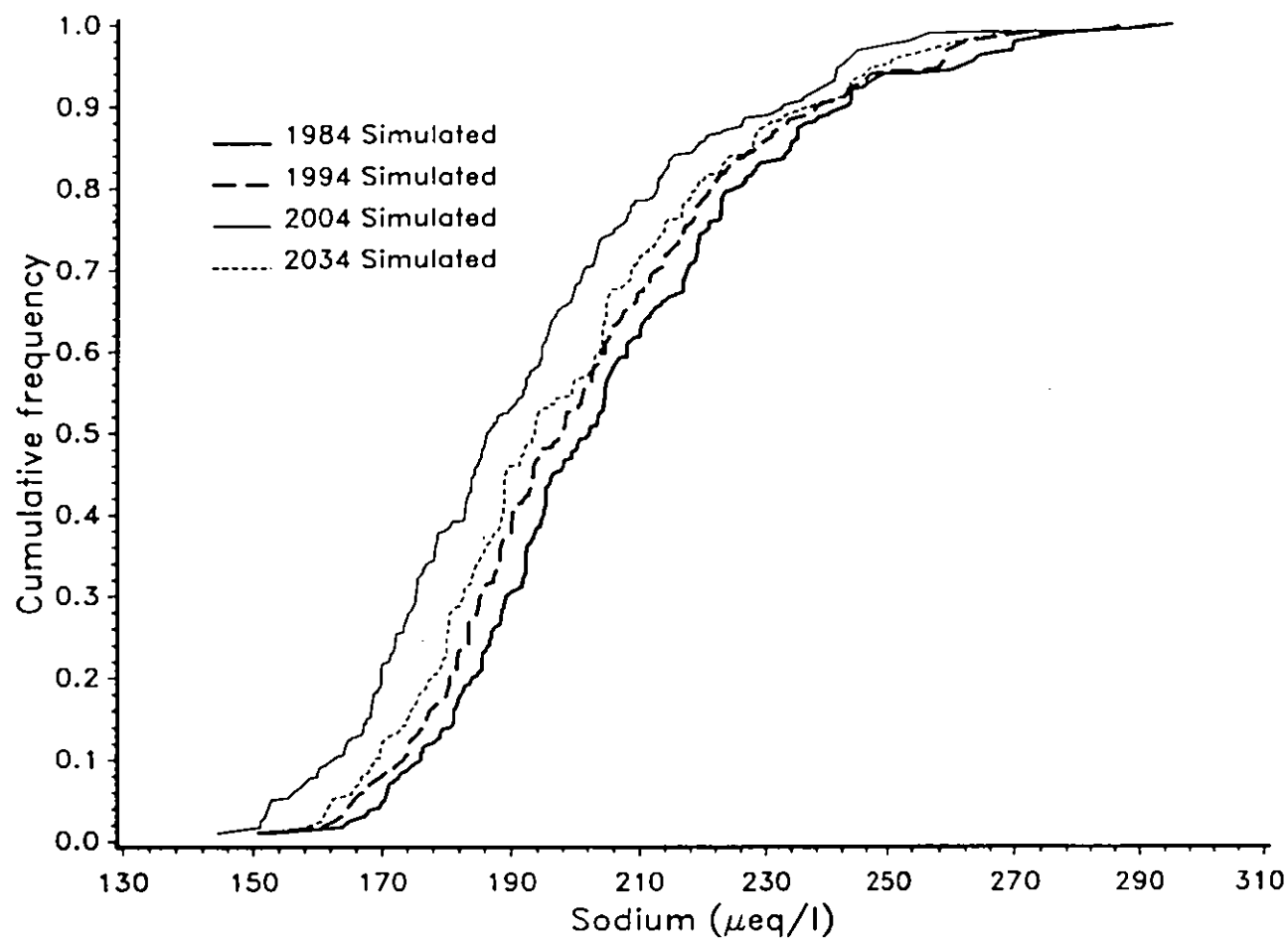


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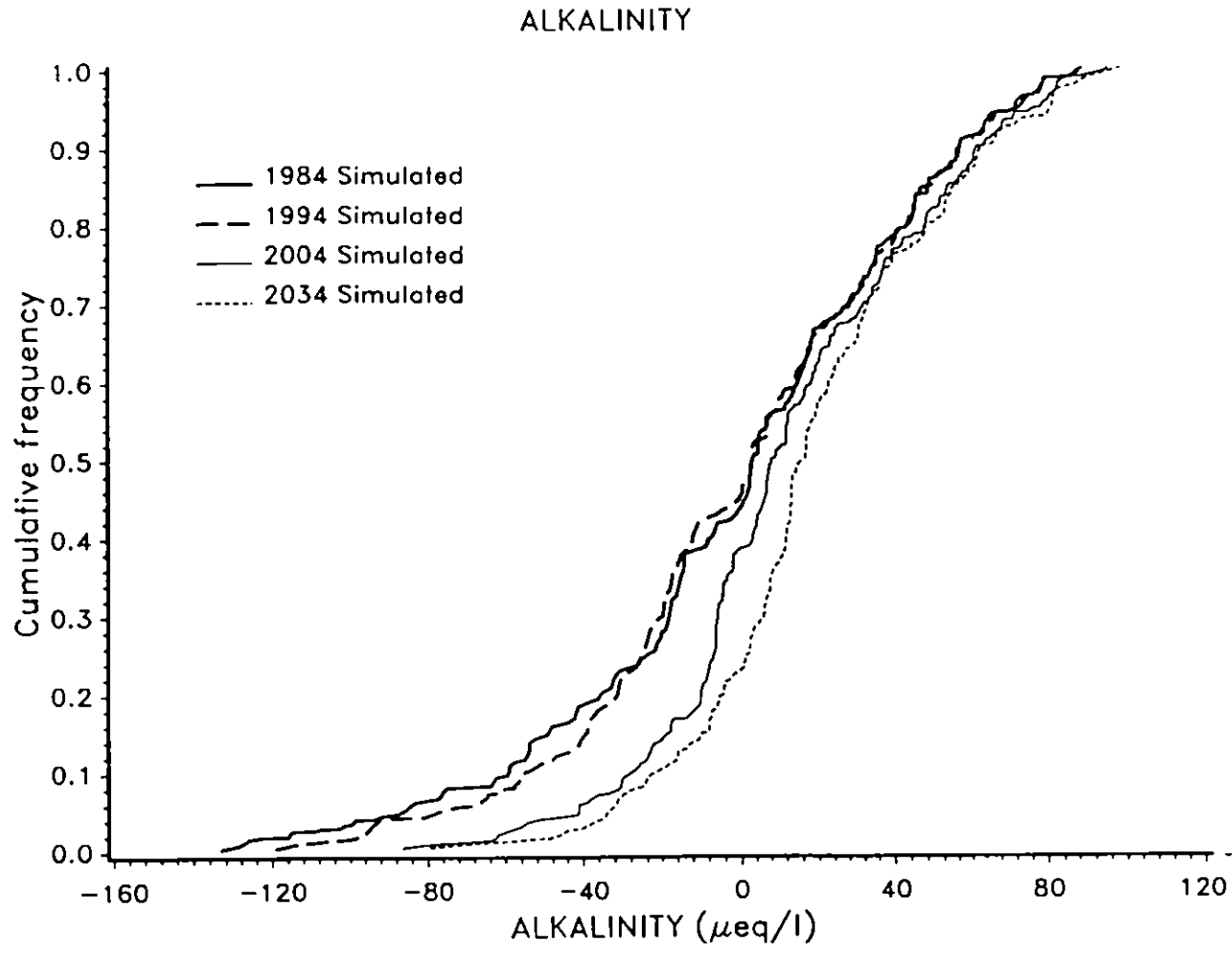


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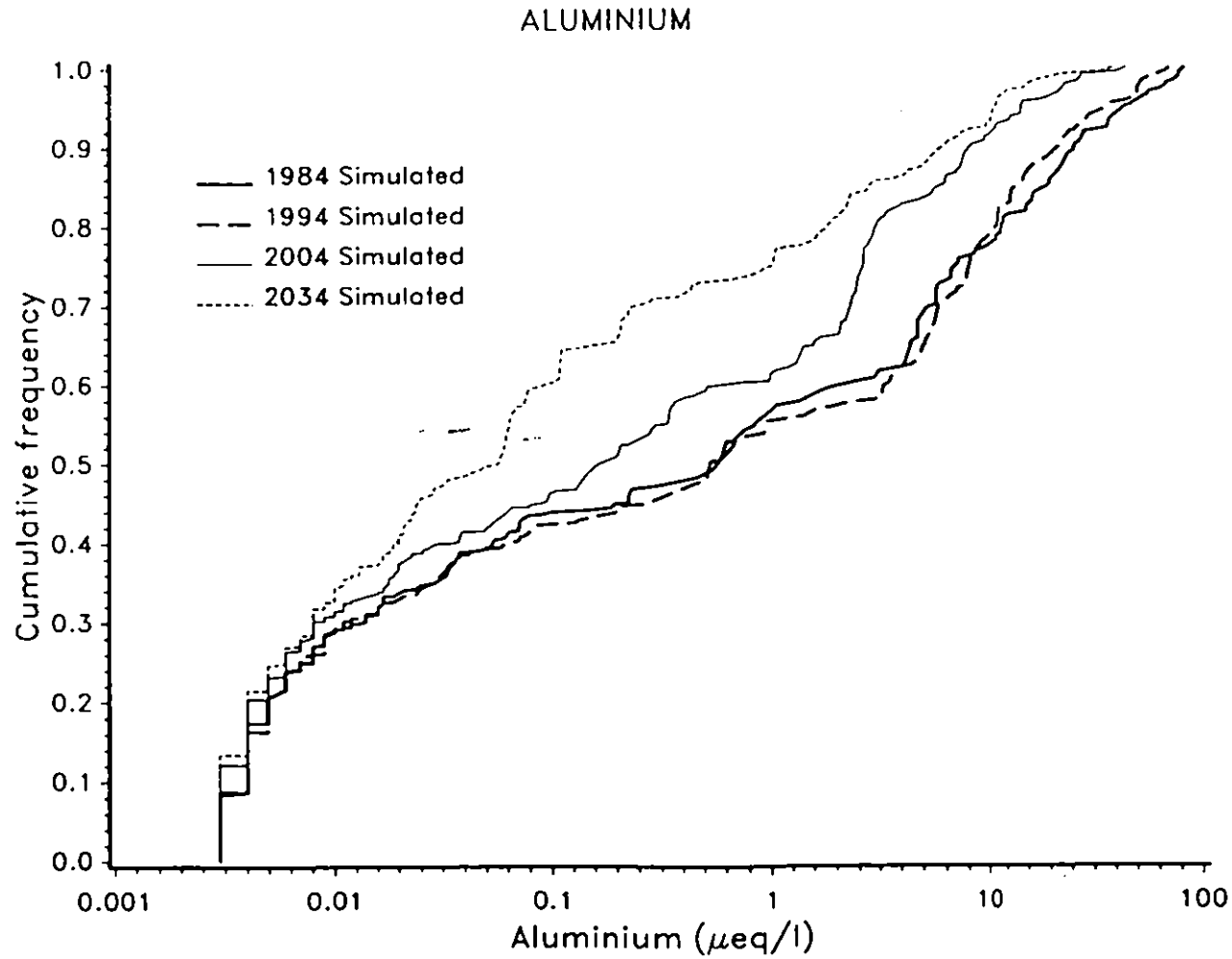


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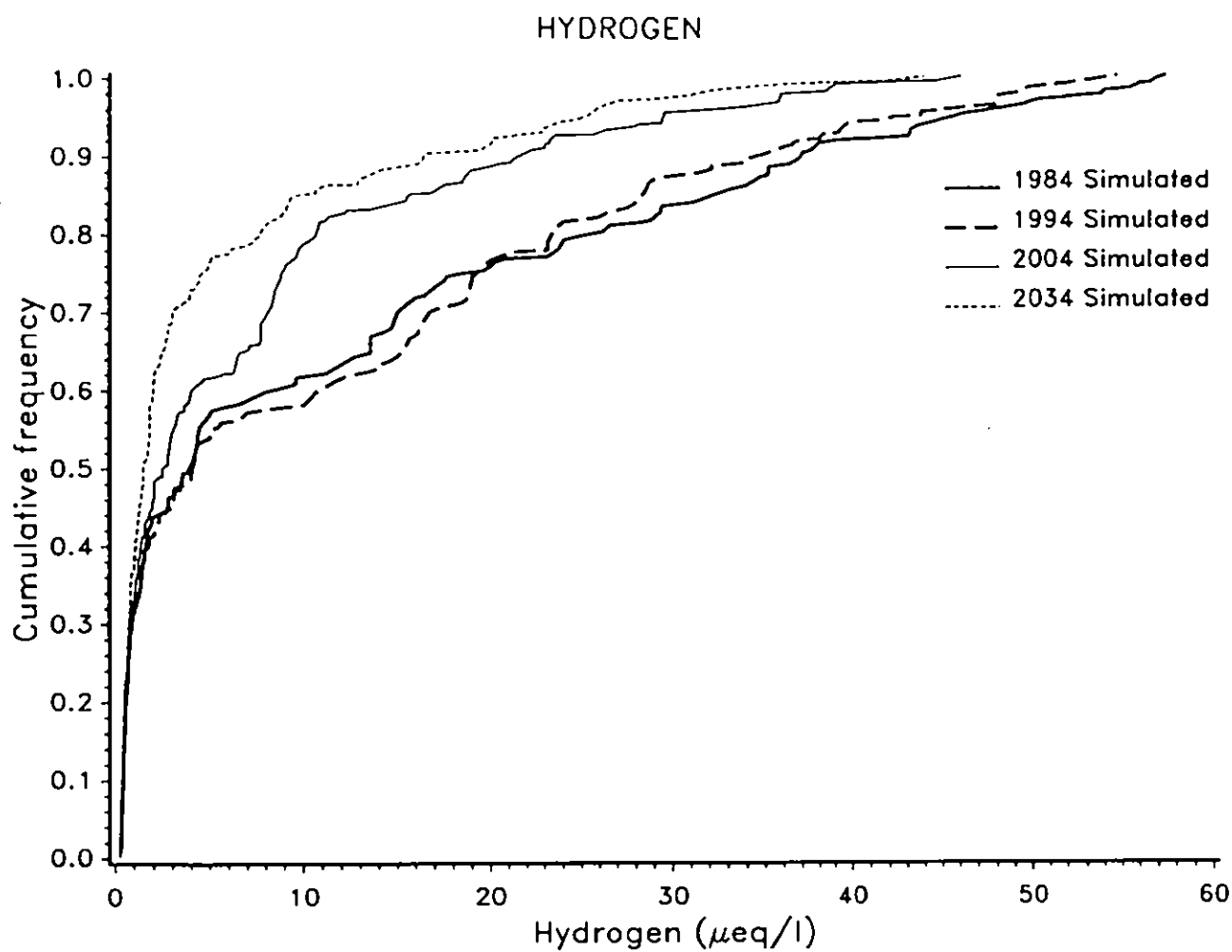


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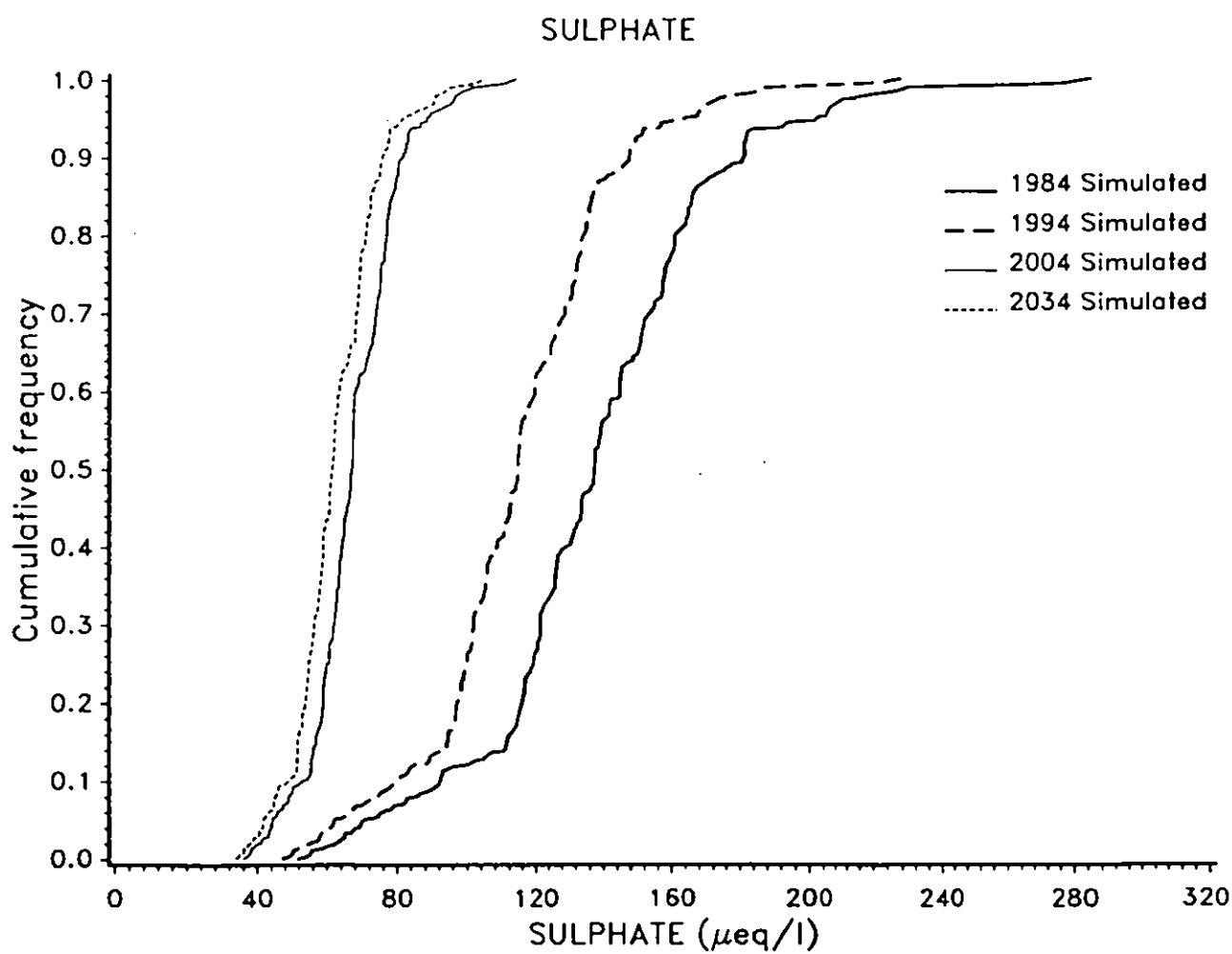


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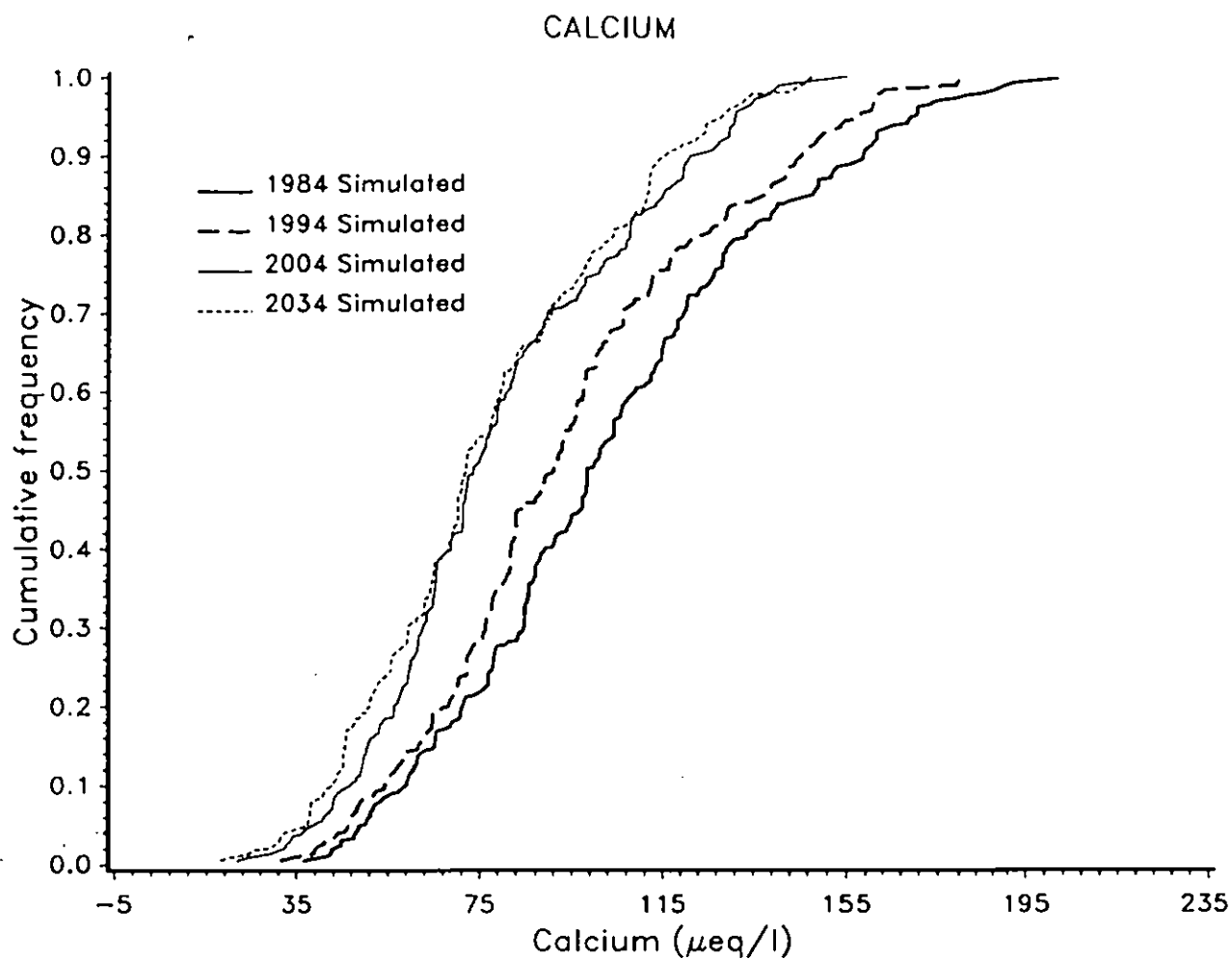
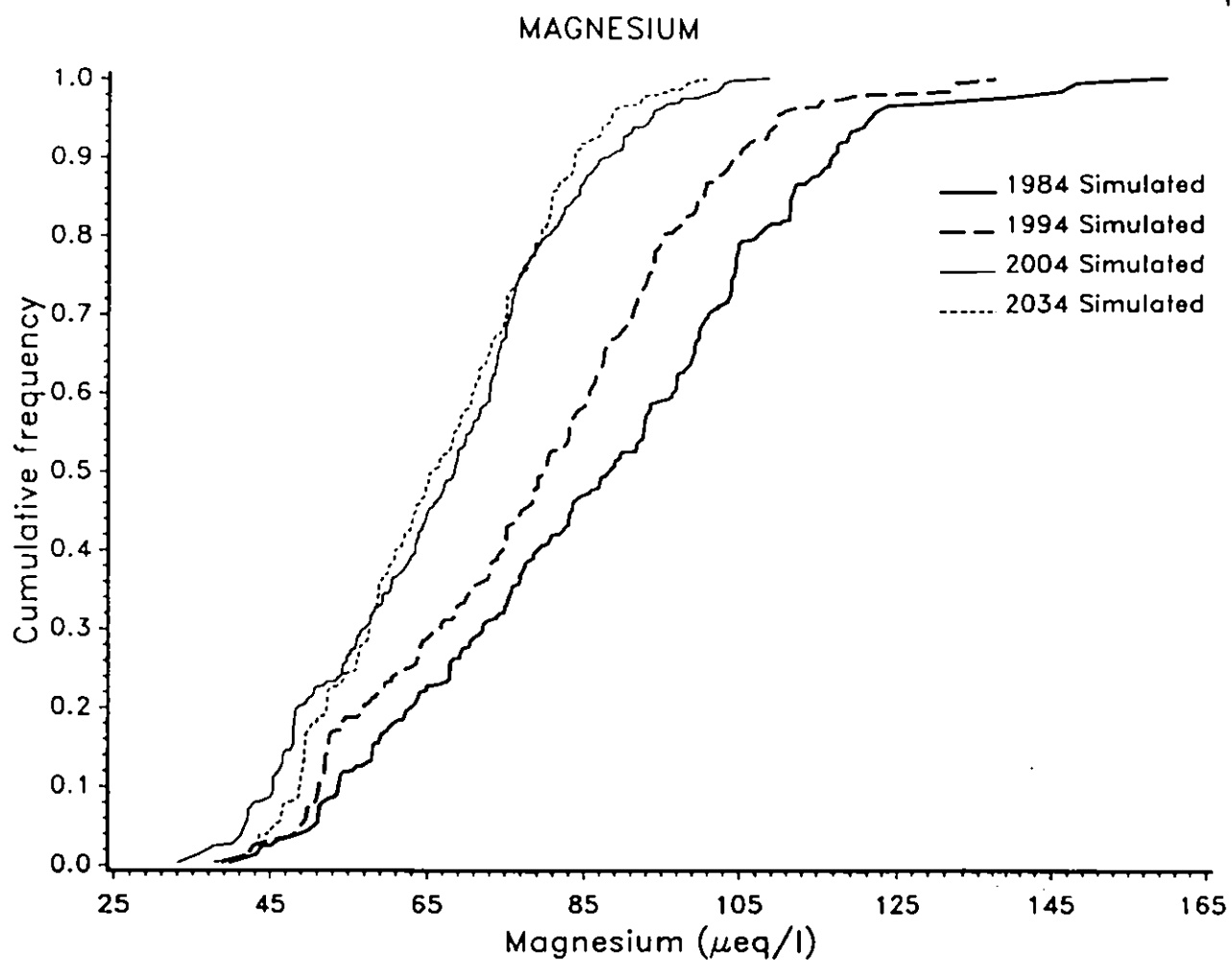


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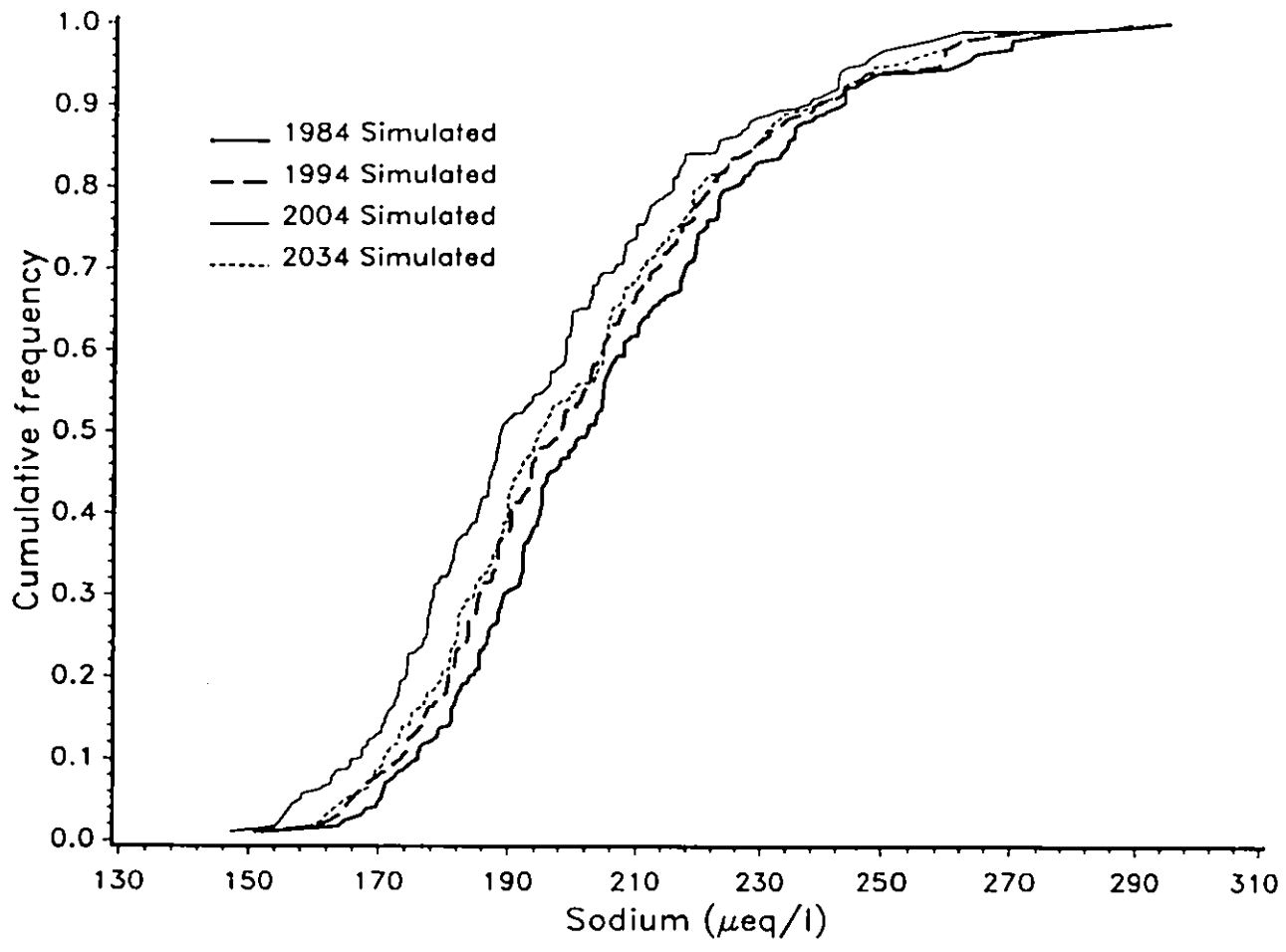


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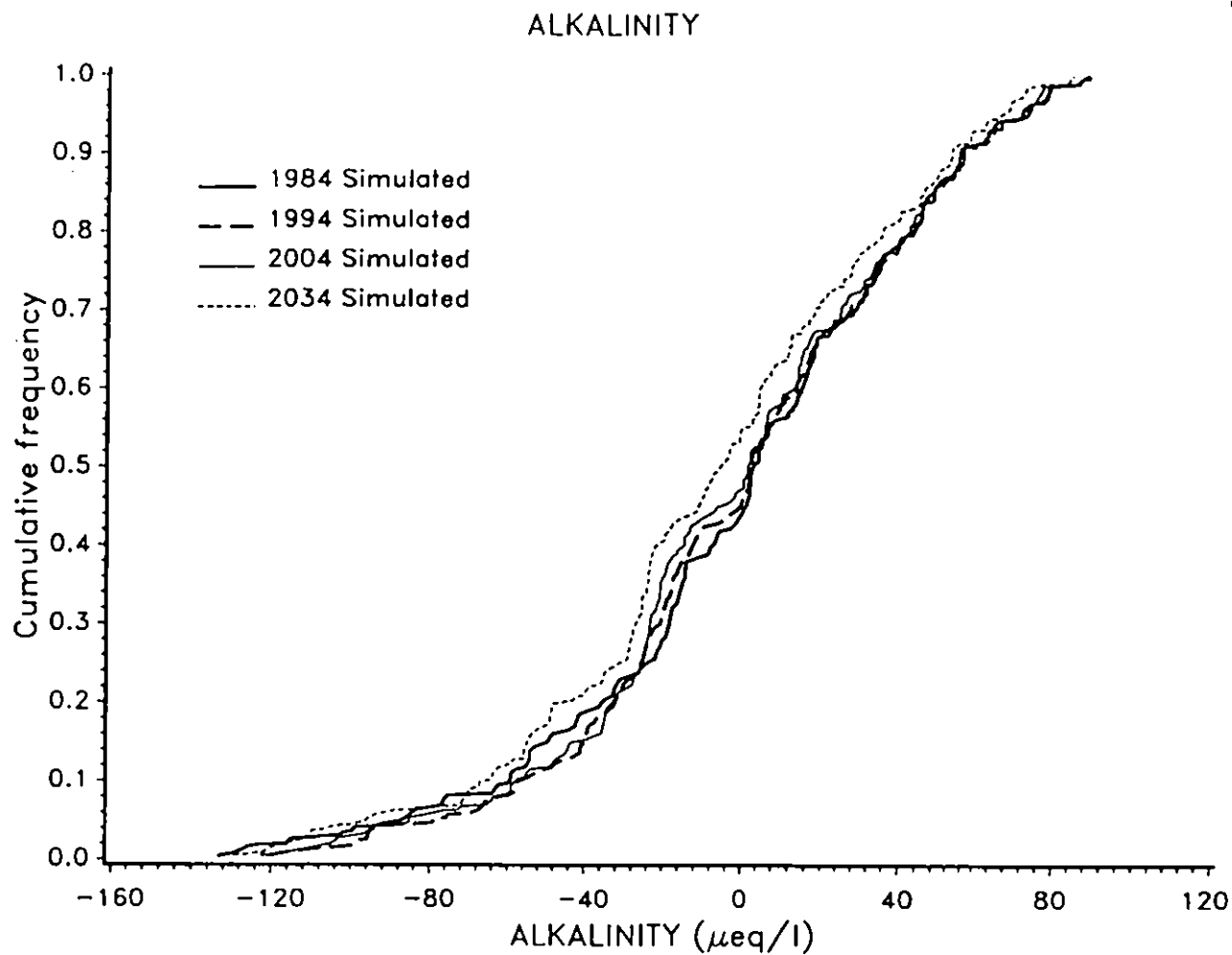


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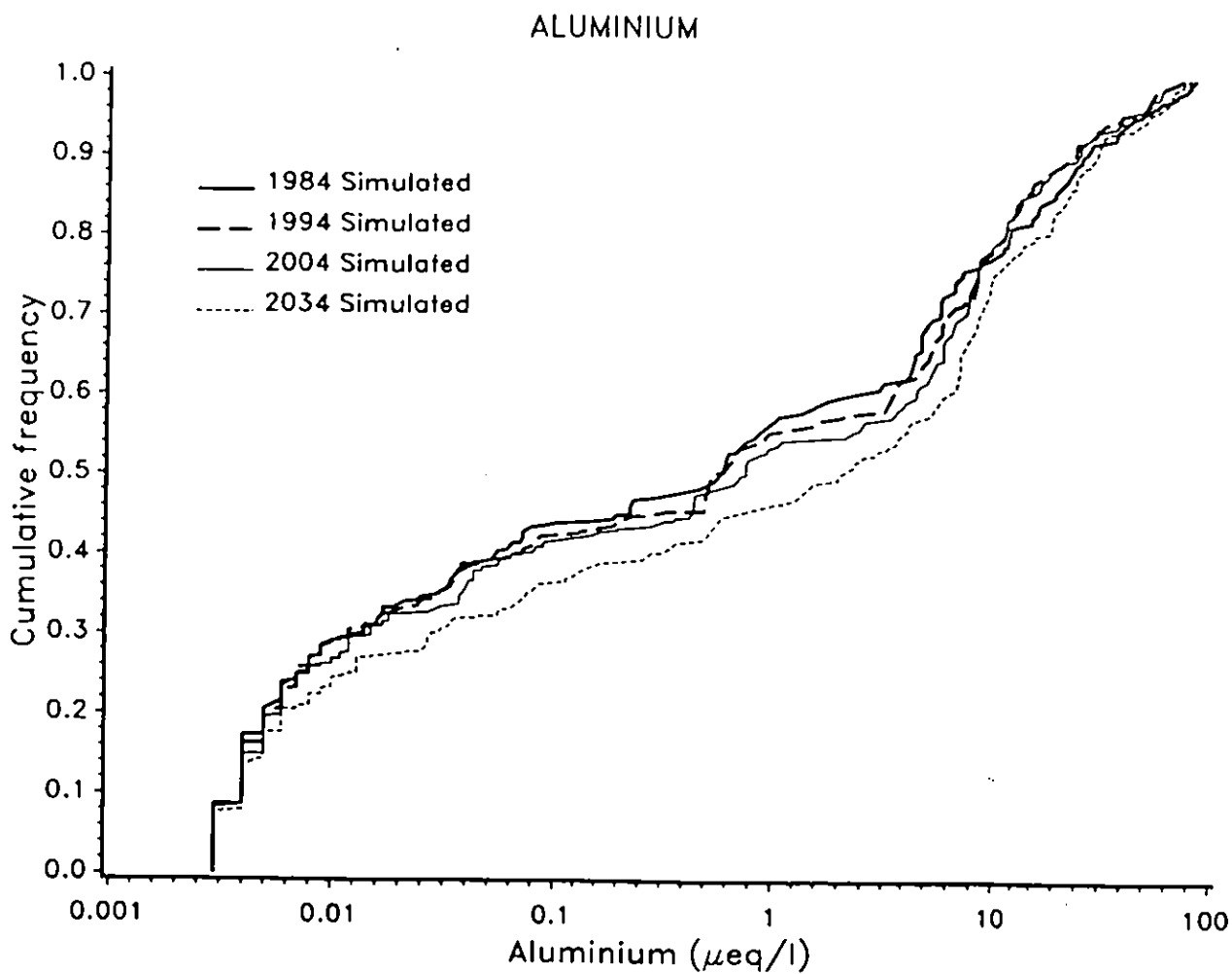


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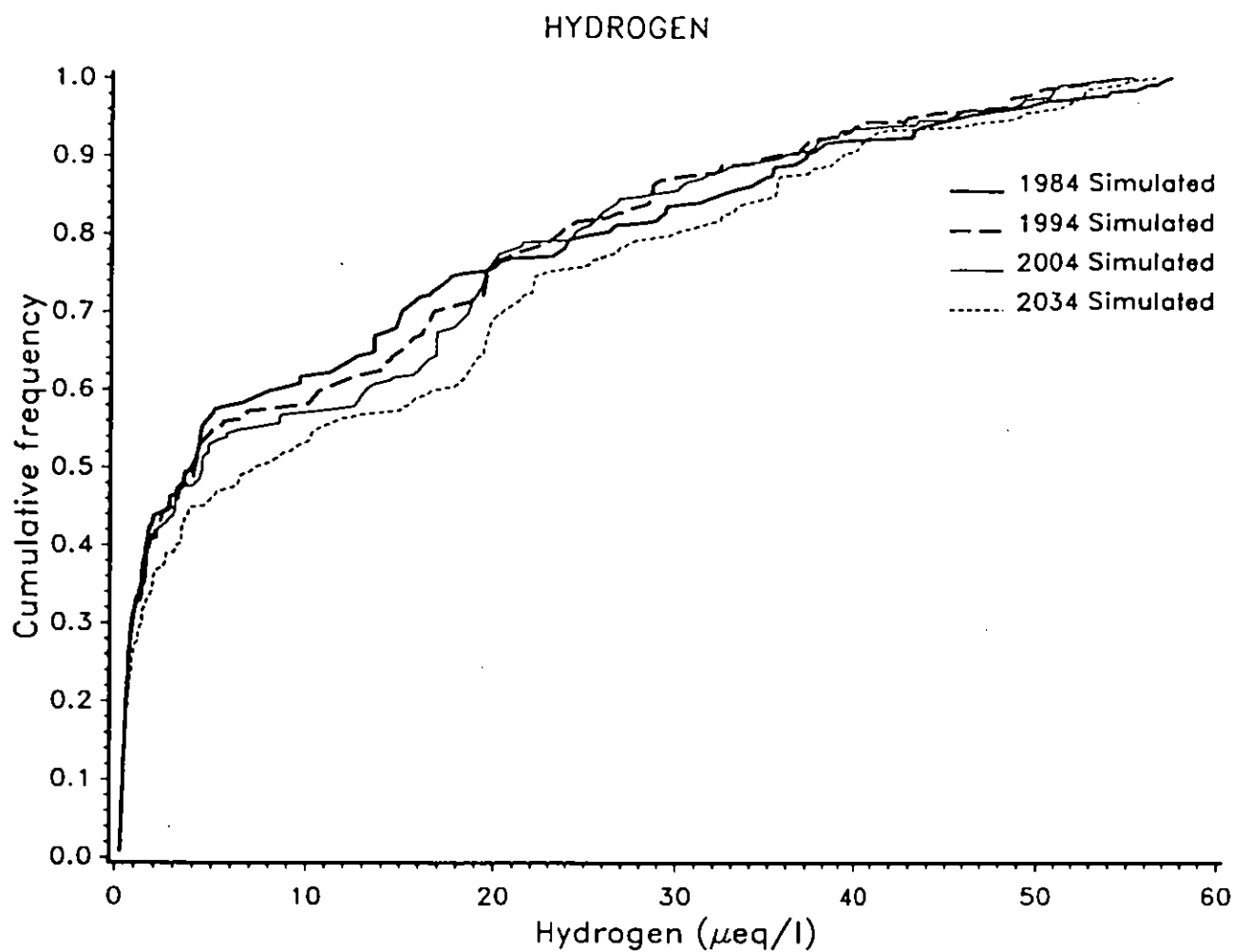


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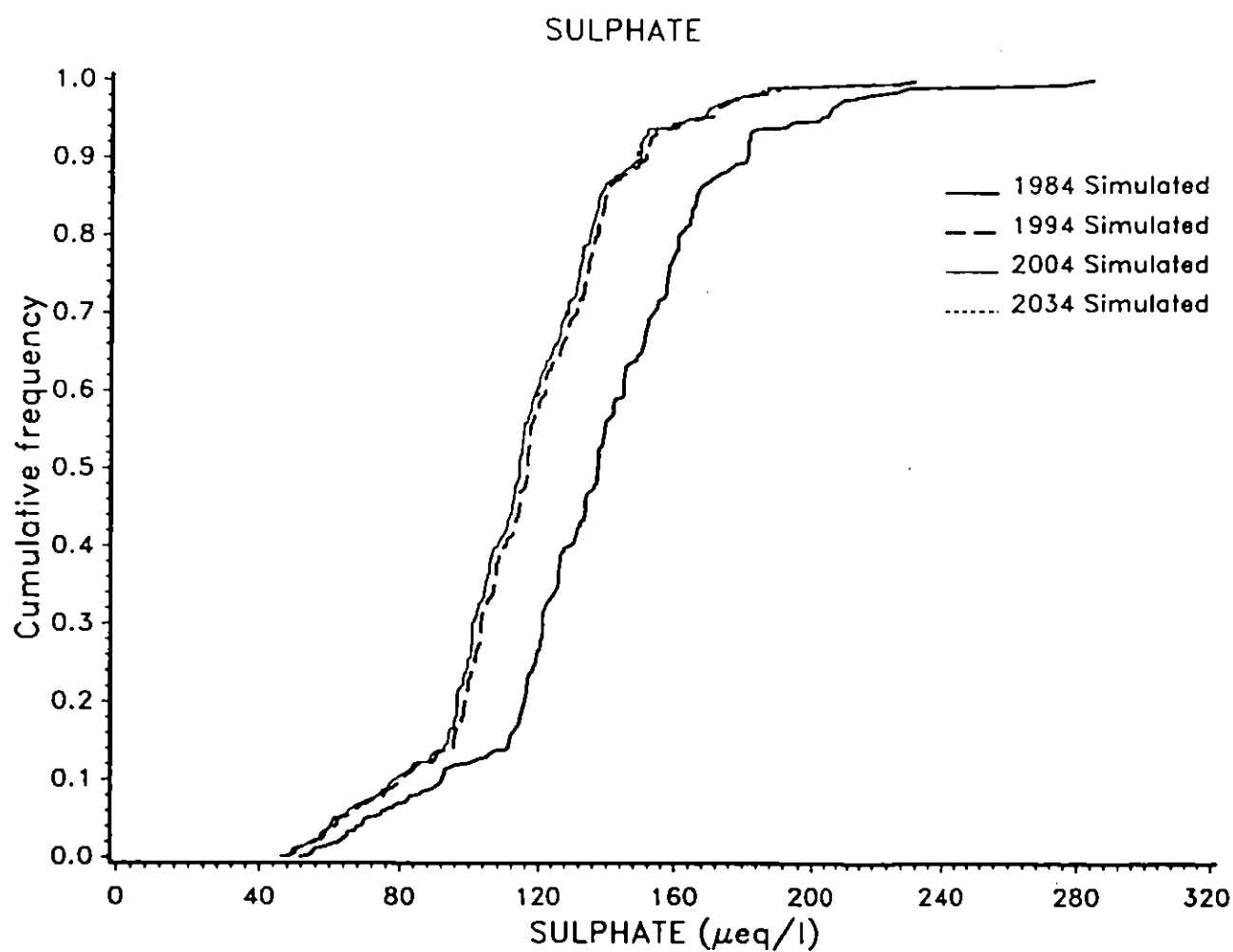


Figure 9 (e)

CALCIUM

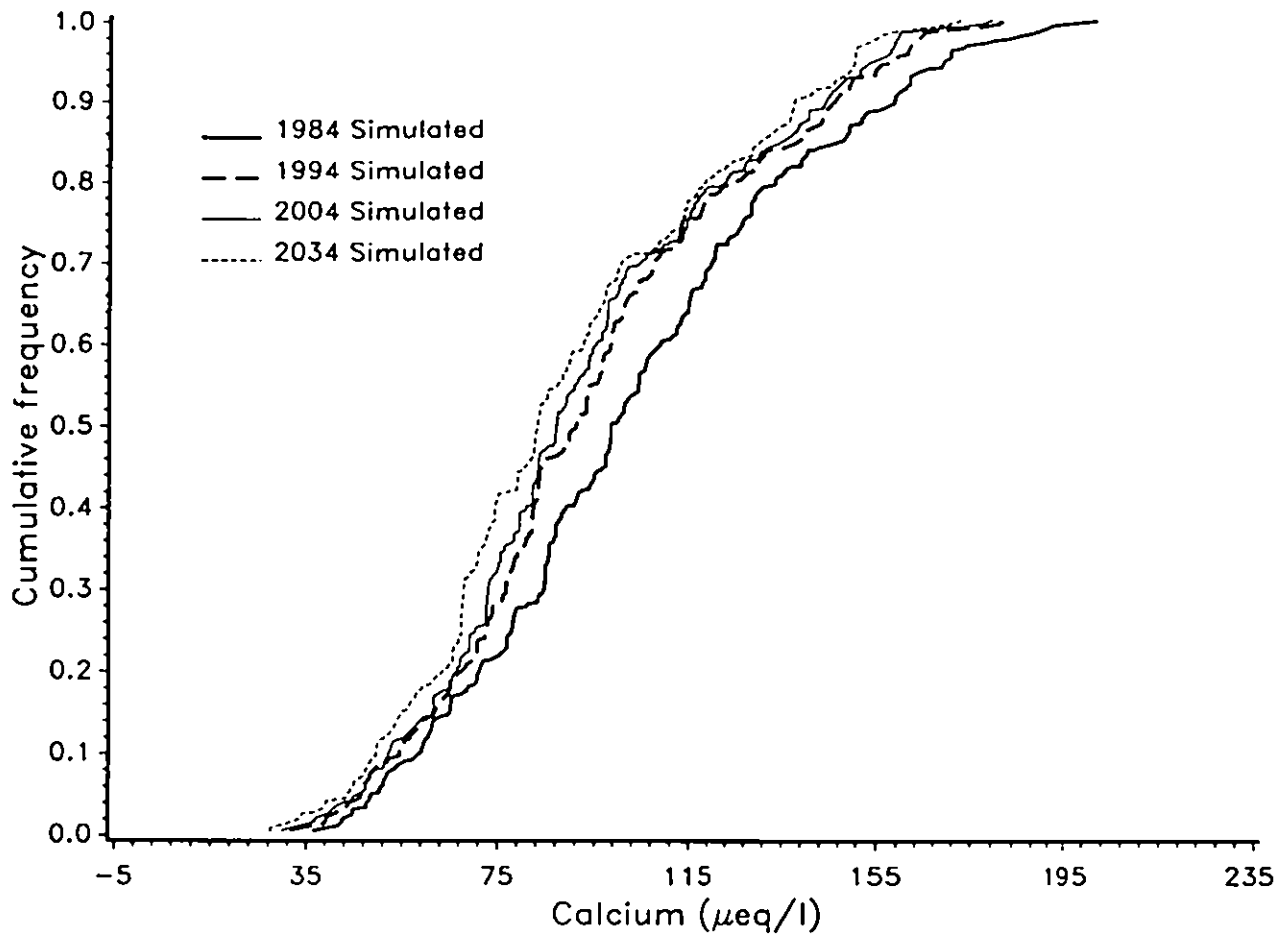
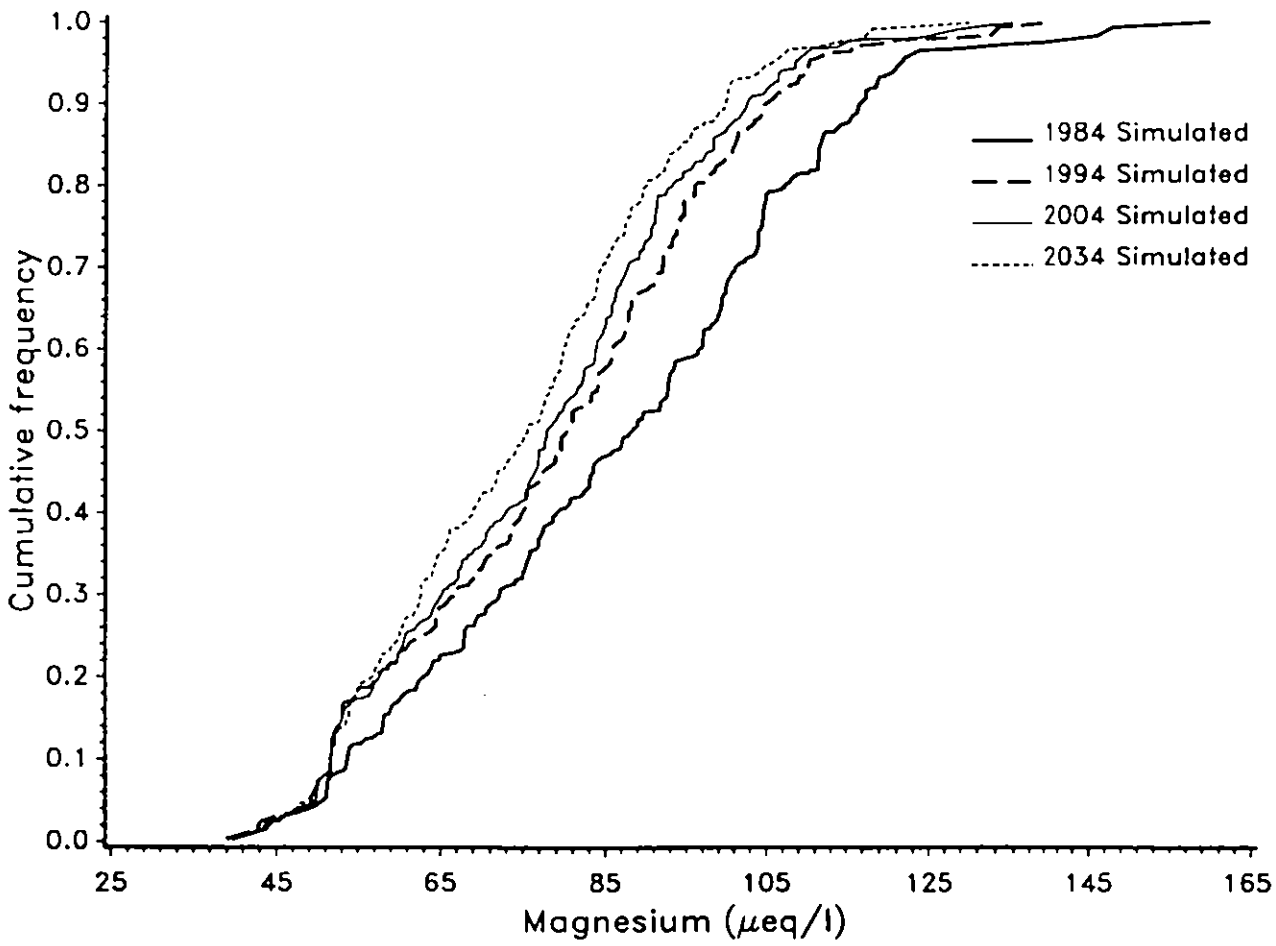
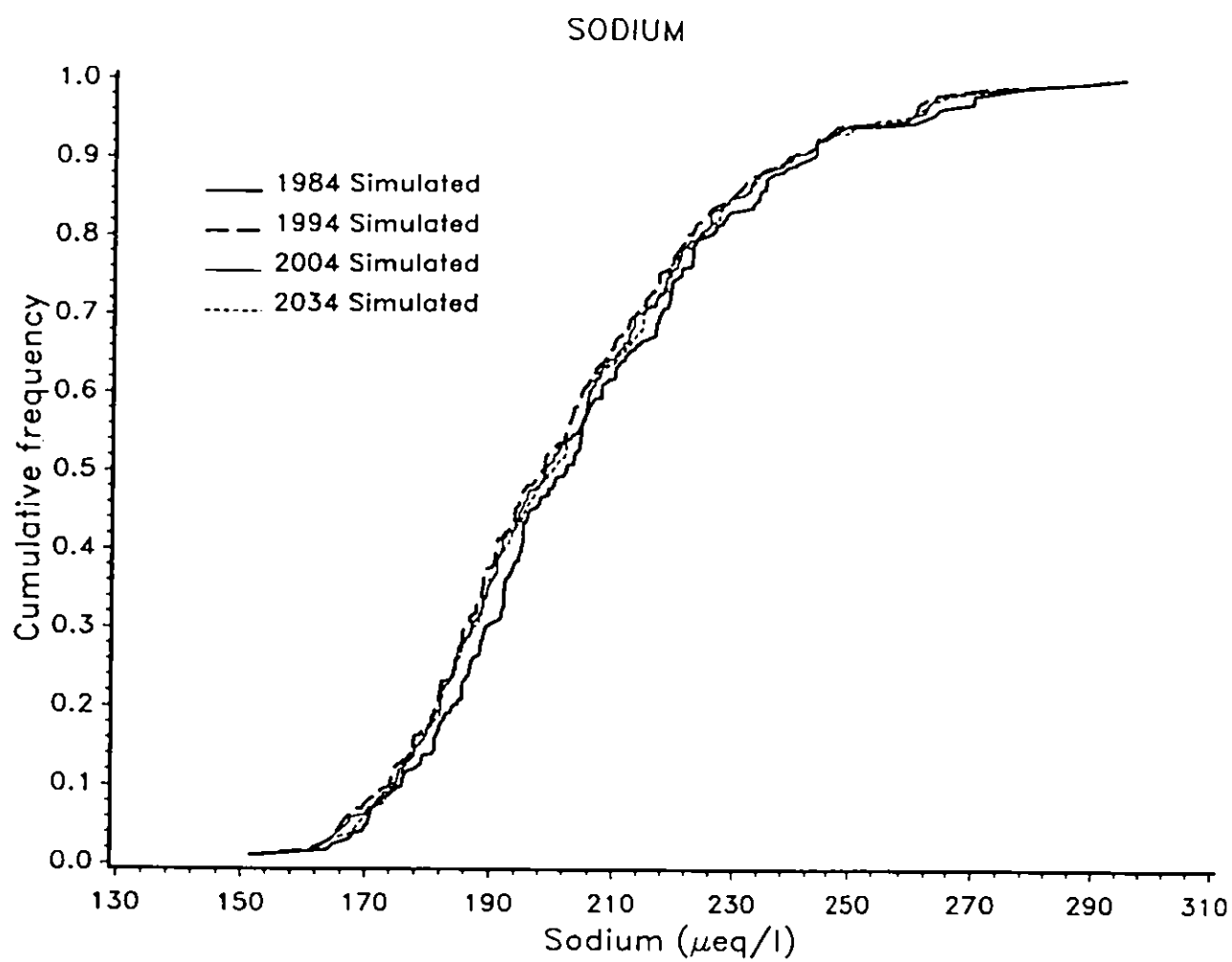


Figure 9 (f)

MAGNESIUM





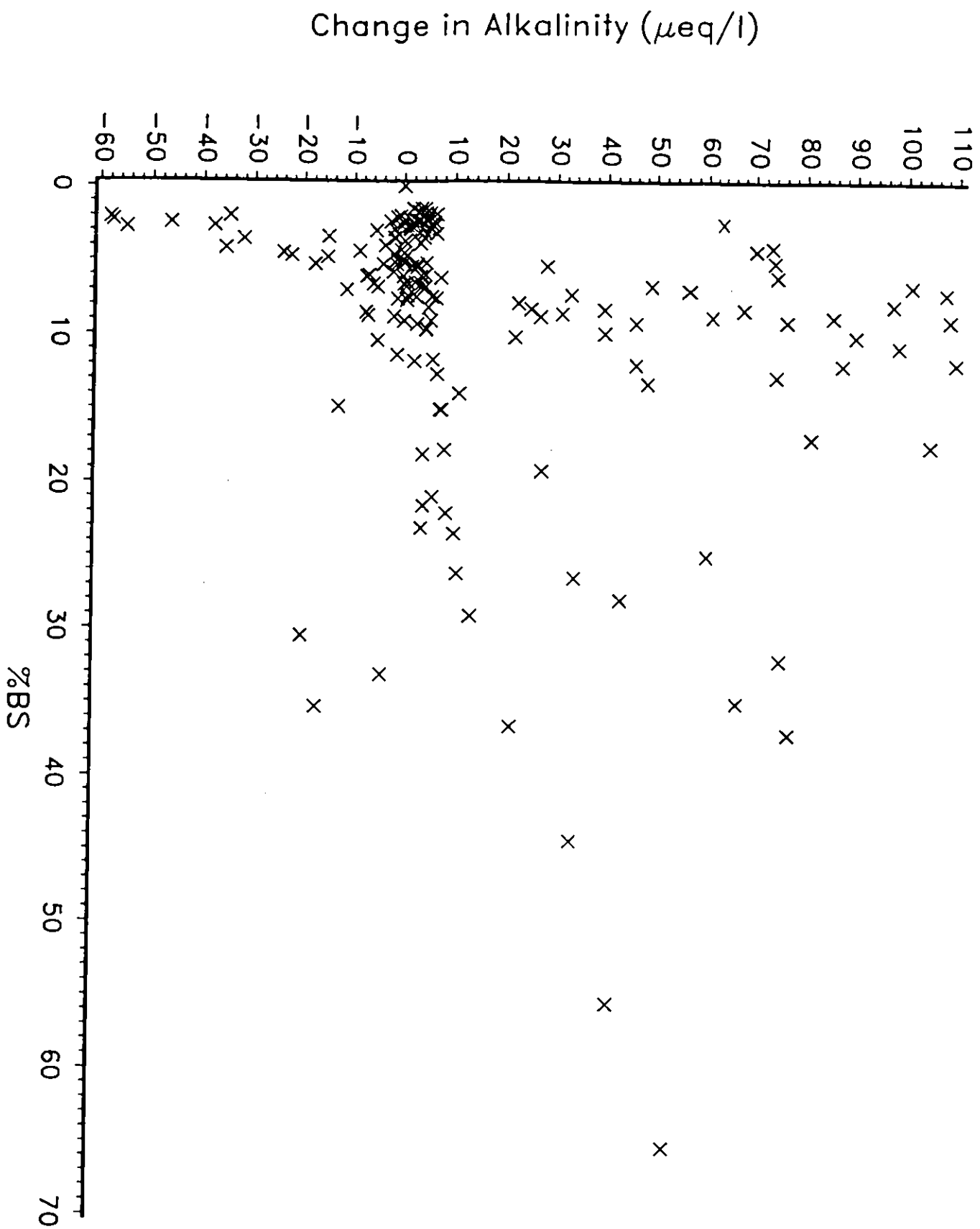


Figure 10

Figure 11 (a)

Nant Y Gronwen

Sensitivity Analysis (Constant Depn)

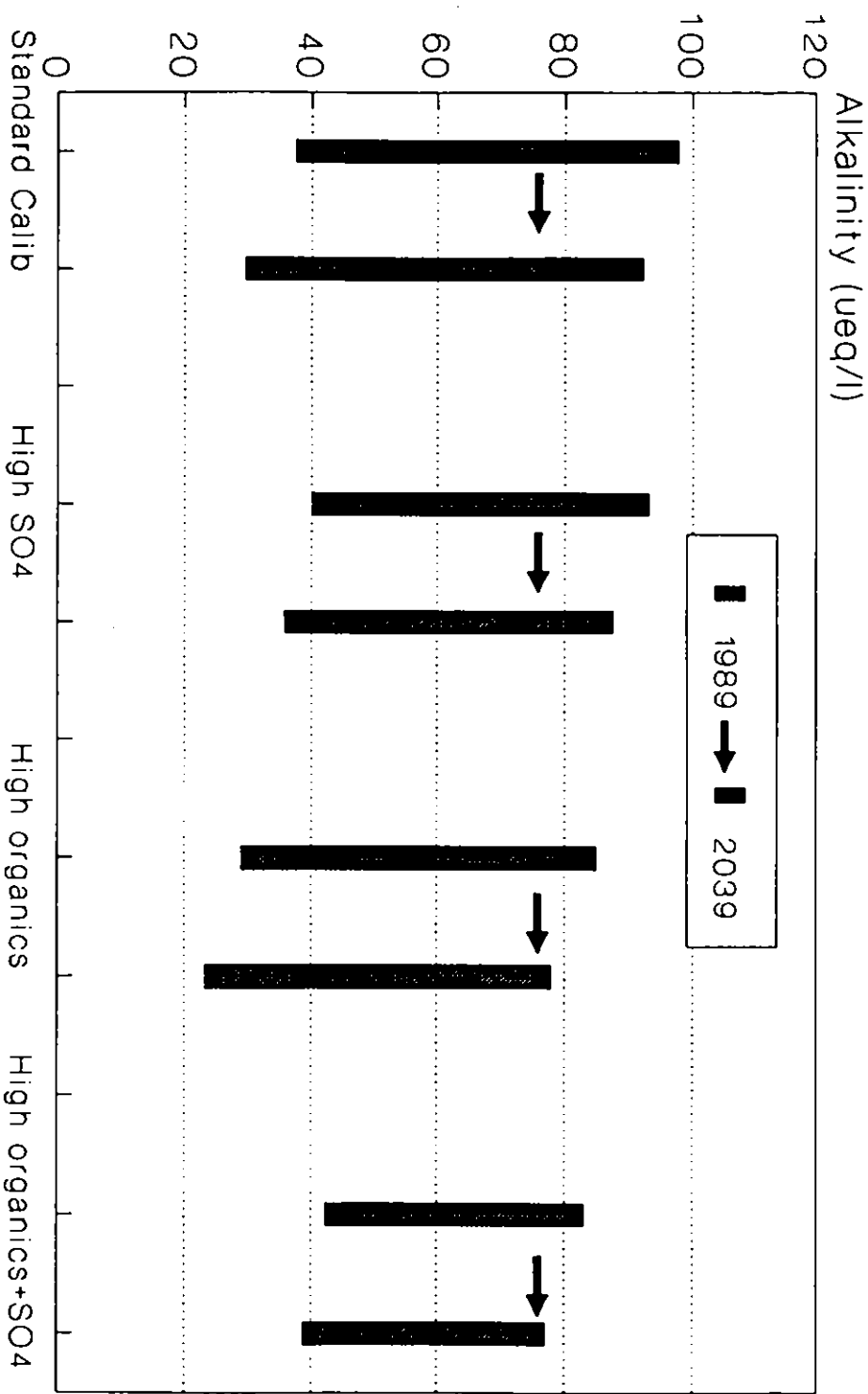
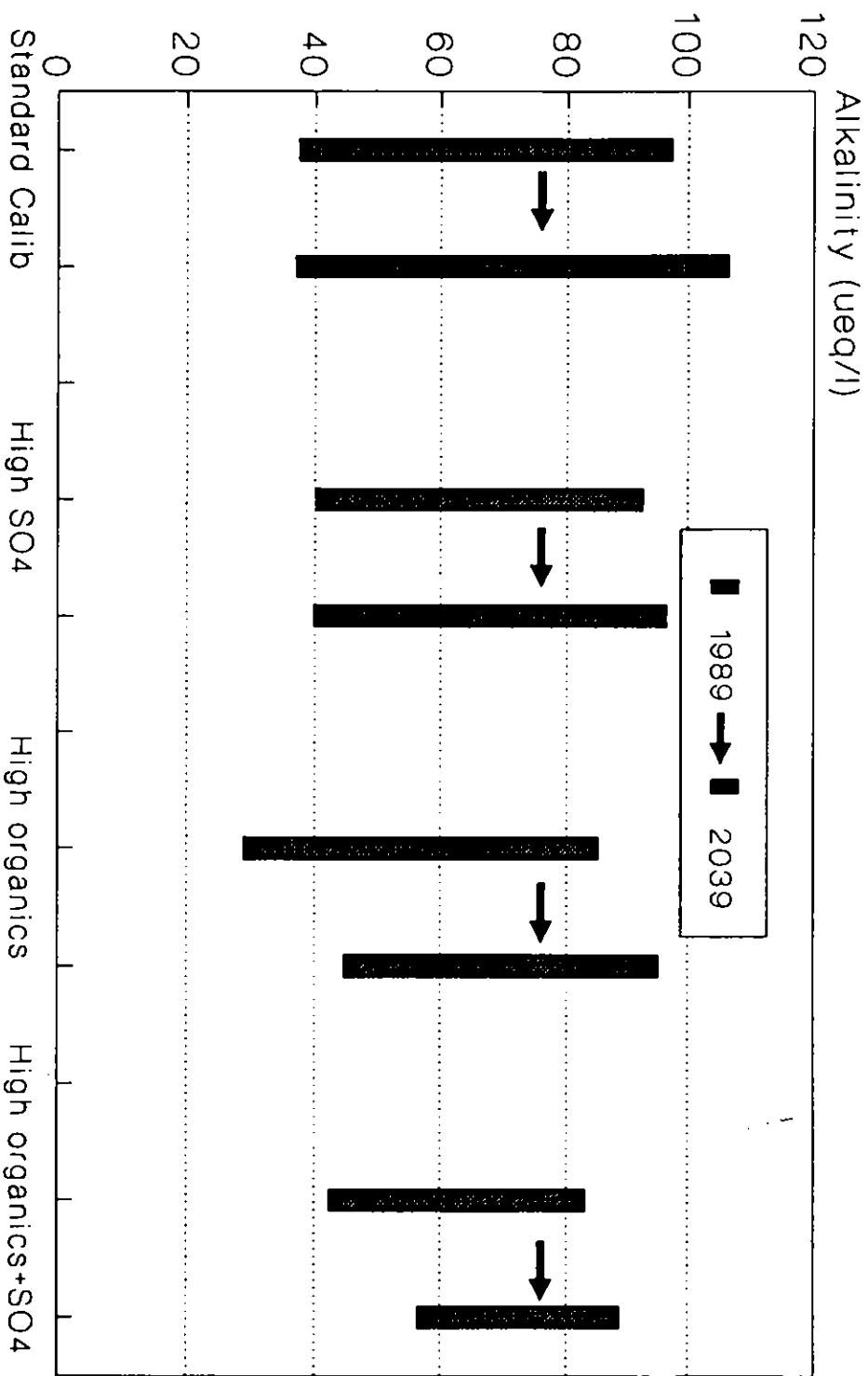


Figure 11 (b)

Nant Y Gronwen

Sensitivity Analysis (LCPD Depn)



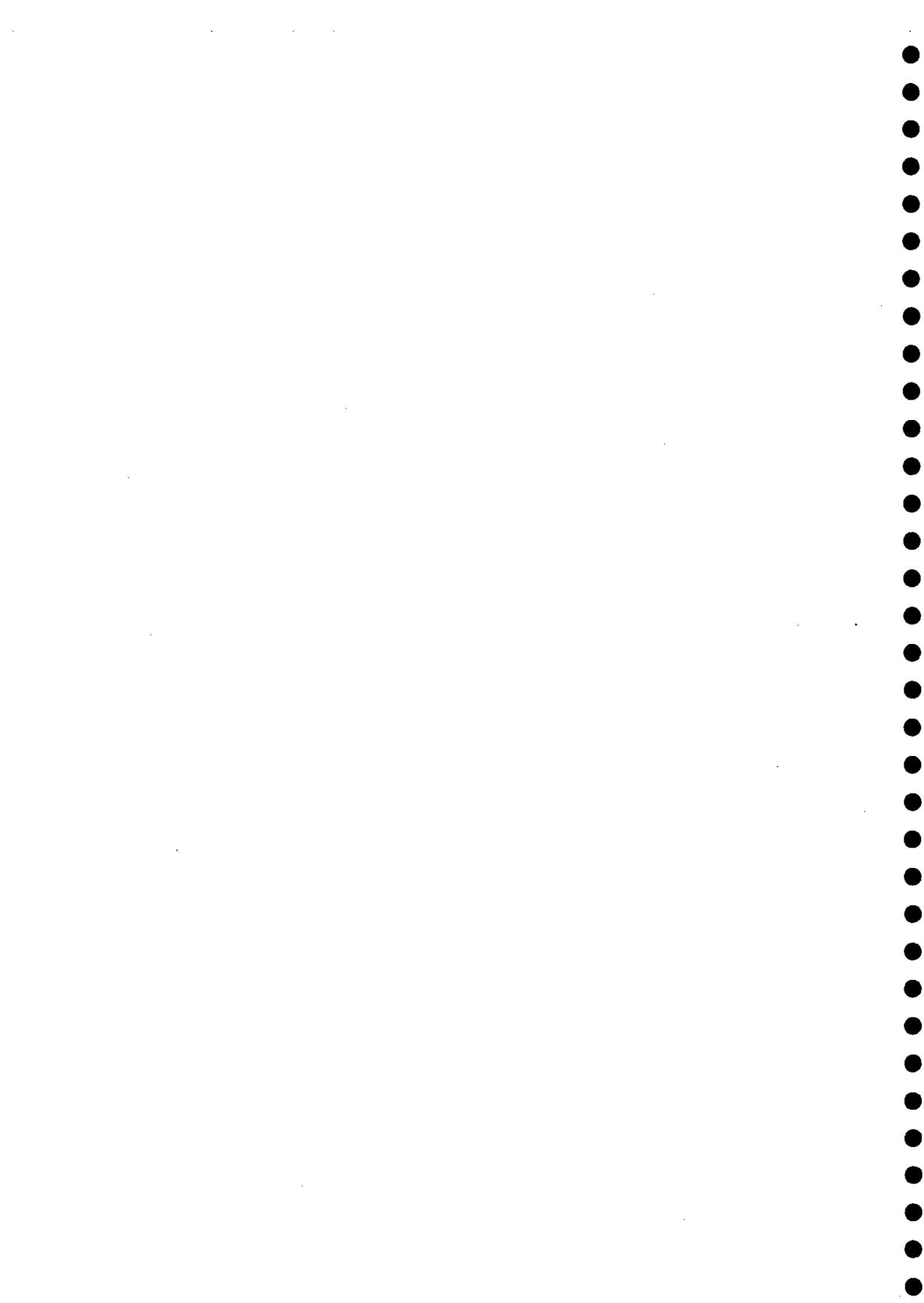


APPENDIX A

A Regional Model of Acidification in Wales

A. Jenkins, P.G. Whitehead, T.J. Musgrove and B.J. Cosby

Journal of Hydrology 116, 403 - 406



[3]

A REGIONAL MODEL OF ACIDIFICATION IN WALES

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ABSTRACT

Jenkins, A., Whitehead, P.G., Musgrove, T.J. and Cosby, B.J. 1990. A regional model of acidification in Wales. *J. Hydrol.*, 116: 403–416.

A regional assessment of streamwater quality in Wales is presented which reconstructs the historical trend for acidification and predicts the effect of several pollutant deposition reduction policies, using the model of acidification of ground water in catchments (MAGIC). The regional methodology used is a two-stage coupling of Monte Carlo simulations with a calibration procedure designed to produce a coarse fit to the joint distribution of the key streamwater quality variables. The regional model is based on data from the Welsh Water Authority Survey of 1983–1984 during which streams and lakes were sampled weekly for one year. The modelling results reveal a significant decline of water quality across the region since industrialization. The model indicates that 40% of the streams and lakes within the region have suffered a decline of mean annual pH of > 0.5 pH units. Predictions indicate that a 30% reduction of deposition would maintain present-day stream quality levels. Reductions of the order of 60% are required to ensure a significant recovery at most sites across the region.

INTRODUCTION

There is now considerable weight of evidence linking emissions of sulphur and nitrogen compounds with acidification of surface water and soil. A need to identify the acid sensitive areas still exists, however in order to assess the potential environmental damage and to investigate methods to halt or reverse the trend in affected areas. Two methods have been highlighted as being capable of relieving the impact of acidification: (1) a reduction in the emission of pollutants; and (2) addition of a neutralizing agent to sensitive sites. The prescription of the most effective remedy requires assessment of the different management strategies proposed in terms of financial and environmental costs.

An important link between emissions and ecological impact is the transmission of acidity from deposition to stream and lake waters. This focuses upon the chemical status of soil matrix and soil water which greatly affect streamwater quality. The soil accumulates changes induced by the addition of pollutant through time emphasizing the importance of historical trends for emission and deposition. These trends must be incorporated into any

estimation of the rate and magnitude of acidification, and the likely recovery. The complexity of the problem necessitates the use of mathematical models for accurate evaluation of management strategies. These models must represent the key processes influencing the long-term acidification of the soil and must be applicable for long-term regional analyses. We use the model of acidification of ground water in catchments (MAGIC) for long-term prediction of soil and water acidification across a region. MAGIC is a soil-based model which represents the processes of major importance to soil acidification and is driven by acid deposition trends (Cosby et al., 1985a,b). The results of the MAGIC model have been used to drive biological models of trout density and survival, and invertebrate species (Ormerod et al., 1988). The model has been widely applied to individual sites in Scotland, North America and Europe and accords well with historical pH reconstructions derived from diatom assemblages (Jenkins et al., 1990). This study uses MAGIC to make a regional simulation of the acid sensitive areas within Wales and to make a preliminary assessment of the ability of the region to recover.

DESCRIPTION OF SURVEY REGION

The study area is underlain by rocks of Cambrian, Ordovician and Silurian age. In the upland areas the soils are thin and base-poor; the combination of rocks resistant to weathering and thin, poor soils gives the region its vulnerability to acid deposition. Evidence of acidification in Wales has been derived from studies of fisheries, forest and moorland soils, geology and hydrochemistry (Stoner et al., 1984; Hornung et al., 1986). In 1984 the Welsh Water Authority investigated the extent of surface-water acidification throughout Wales by conducting a survey of streams and rivers. The area sampled was selected as being the region of greatest acid susceptibility (Fig. 1). During the same period, rainfall quality was monitored at 44 sites throughout Wales. The mean annual rainfall concentrations are summarized in Table 1. A breakdown of the results by region shows the most acidic rainfall in the uplands of Mid-Wales and North Wales (Donald and Stoner, 1989). The east of Wales receives the highest concentrations of SO_4 and NO_3 ; it also receives high levels of NH_4 and Ca, which partially buffer the rainfall. Mean pH across the region varied from 4.4 to 5.0.

Mean annual stream chemistry is presented in Table 2. The pH of streams varies across the region from 4.2 to 7.3 with a mean of 5.6. The very high maximum Ca level of $862 \mu\text{eq l}^{-1}$ and the maximum Mg concentration of $393 \mu\text{eq l}^{-1}$ were both measured at the site on the Isle of Anglesey where there is a large Al smelter. At this site, the alkalinity is also a maximum for the region at $1104 \mu\text{eq l}^{-1}$.

The mean annual Na and Cl levels are strongly correlated ($R^2 = 0.93$) and sea-salt concentrations are high. The area is mountainous and rainfall is high with a large orographic input. The predominant weather pattern sweeps westerly air from the Atlantic Ocean and the Irish Sea over Wales. The high

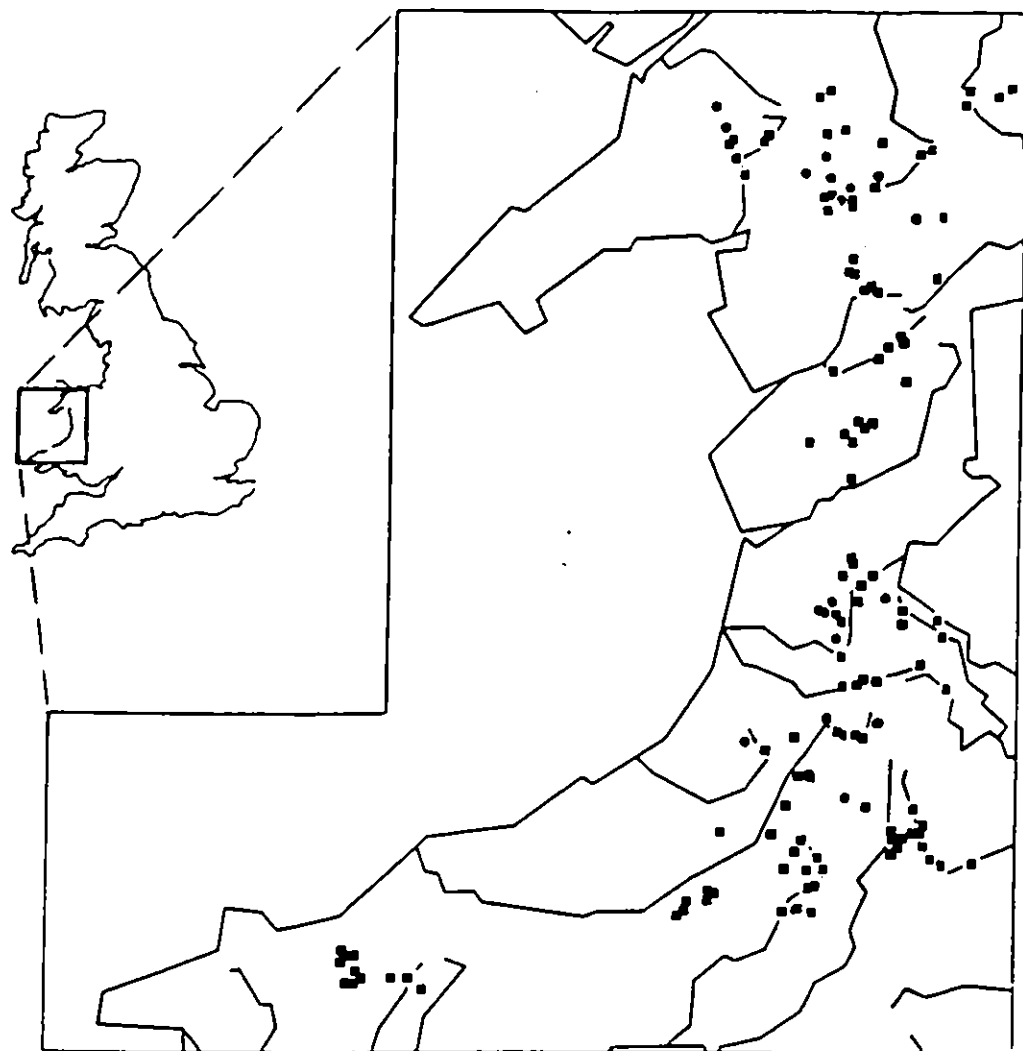


Fig. 1. The study region and sampling locations

mean SO_4 concentration in the streams includes a large component in excess of SO_4 of marine origin. The presence of the SO_4 in the streams is balanced by base cations in the well-buffered catchments and by hydrogen and Al at the more acidic sites.

TABLE 1

Rainfall chemistry ($\mu\text{eq l}^{-1}$ except pH) at 44 sites in Wales 1983–1984

	<i>N</i>	Mean	Median	Standard deviation	Minimum	Maximum
pH	44	4.7	4.7	0.56	4.4	5.0
Ca	44	47.7	41.0	38.6	9.9	102.2
Mg	44	42.6	33.4	43.8	17.4	177.8
Na	44	137.0	124.5	171.2	62.5	510.9
K	44	8.6	7.3	5.4	4.7	21.8
SO_4	44	118.7	110.8	34.3	52.0	217.1
Cl	44	176.1	162.1	192.5	96.8	525.0
HCO_3	44	51.3	38.7	49.9	22.9	114.9

TABLE 2

Mean annual stream chemistry for the 130 sampling sites in the Welsh regional survey

	Mean	Standard deviation	Minimum	Maximum
pH	5.6	0.7	4.2	7.3
Ca	130.9	91.7	40.4	862.3
Mg	111.5	113.4	44.4	393.2
Na	220.1	62.0	149.1	640.0
K	13.4	9.8	5.4	89.0
SO ₄	153.7	64.4	49.1	507.4
Cl	267.4	86.2	167.0	918.0
HCO ₃	75.5	87.3	0.7	604.1
H	1.9	3.4	0.05	24.0
Alk	30.6	125.4	-206.9	1103.9
pCO ₂	7.25	7.6	1.0	51.2
Al _T	6.3	4.3	0.7	24.3

Units are $\mu\text{eq l}^{-1}$, except Al ($\mu\text{mol l}^{-1}$), pH and pCO₂ (atmospheres $\times 10^{-3.5}$).

REGIONAL APPLICATION OF THE MAGIC MODEL

The MAGIC model may be adapted for modelling on a regional basis by the introduction of Monte Carlo techniques which assimilate regional variability. Weathering rates for base cations, soil depths and porosities, rainfall, cation exchange capacities, exchangeable base fractions on cation exchange sites, and chemical inputs from precipitation will vary across the region. In the model these factors are each represented by a model parameter and the Monte Carlo technique allows the parameters to vary across a wide range. The essence of the technique is to run the model repeatedly until sufficient information is obtained. For each of a large number of model runs, random values of the parameters are drawn from previously defined population distributions. When a sufficient number of successful runs are completed the calibrated set of model runs has a distribution of parameters that matches the distributions of the observed equivalents. Any knowledge of the likely covariation of parameters may be built into the model by specifying joint distributions for the varying parameters. For example, if there existed correlations between rainfall and elevation and between depth of soil and elevation, then a relation between rainfall and soil depth may be deduced; usually little is known of the parameter covariation and they are assumed to be independent. The Monte Carlo runs provide many simulations which, if the parameter ranges are sufficiently wide, span the range of observed chemistry across the region. These simulations are employed in a calibration procedure to discard simulations with predictions that are not observed within the region and to tighten the model fit.

To achieve the regional calibration, a large pool of simulations are accumulated and a relative frequency count is made on the observed discrete joint

distributions. Weights are assigned to each simulation to provide a weighted relative frequency count that is identical with the observed. Hornberger et al. (1989) presented a detailed description of this technique.

APPLICATION TO WALES

MAGIC has been applied to several individual sites within the study region (Whitehead et al., 1988a,b), and the calibrated set of parameters for those studies formed the basis of the regional application. A one-soil layer version of MAGIC was used as the added complexity of a two-layer version has not been found to produce significantly different simulations of surface water chemistry (Jenkins and Cosby, 1989). Twelve parameters were subject to Monte Carlo uncertainty (Table 3). The mean precipitation volume per year (Q_p) is assumed to fall uniformly across the region and is held constant throughout the simulation. Variability of Q_p , therefore, incorporates variability of soil depth and porosity to some extent. 15% of the rainfall is assumed to evaporate. The 1984 rainfall concentrations of Cl and excess NO_3 and SO_4 were set for each model run by randomly sampling pre-set distributions. Within the model, Cl is assumed to be conservative and so the rainfall Cl concentration distribution can be calculated from knowledge of the stream Cl distribution and the runoff. Background (1844) precipitation was set equal to the present-day sea-salt concentrations.

The trend of excess SO_4 and NO_3 deposition through time is scaled to present-day deposition levels. The shape of the trend is taken to be equal to the overall mean emission curve for the U.K. reported by Warren Springs Laboratory (1983). The time trend in the remaining chemical concentrations in

TABLE 3

Ranges for the parameters used in the Monte Carlo simulations. The parameters are defined in the text

Parameter	Units	Monte Carlo ranges		Accepted simulations			
		Minimum	Maximum	Weighted mean	S.D.	Minimum	Maximum
Q_p	cm	120.0	230.0	177.3	29.5	122.4	229.8
Cl	$\mu\text{eq l}^{-1}$	167.0	400.0	243.4	34.0	175.8	379.2
SO_4	$\mu\text{eq l}^{-1}$	20.0	225.0	79.7	34.9	20.3	211.0
NO_3	$\mu\text{eq l}^{-1}$	2.4	140.0	46.5	22.0	4.1	125.7
CEC	meq m^{-2}	10.0	300.0	148.7	87.0	10.0	299.4
WE_{Ca}	$\text{meq m}^{-2} \text{year}^{-1}$	0.5	150.0	83.5	38.0	1.1	149.9
WE_{Mg}	$\text{meq m}^{-2} \text{year}^{-1}$	0.5	50.0	21.3	13.9	0.9	49.9
WE_K	$\text{meq m}^{-2} \text{year}^{-1}$	0.5	10.0	5.3	2.7	0.5	9.9
E_{Ca}		0.5	20.0	11.1	5.3	0.6	19.9
E_{Na}		0.5	5.0	2.8	1.3	0.5	0.5
E_K		0.5	5.0	2.7	1.2	0.5	0.5
E_{Mg}		0.5	20.0	9.2	5.9	0.5	19.9

precipitation was determined by using the present-day excess concentrations over sea-salt to scale the trend line. The present-day rainfall concentrations used are shown in Table 1. These concentrations are the same for each model run. Nitrate in the soil was assumed to be taken up by plants at a constant rate of 45% of NO_3 input. A wide variation of the cation exchange capacity (CEC) was used in the Monte Carlo simulations reflecting the high variability of measured data. Each soil horizon within the catchment may have a different CEC value and the lumped model parameter must allow for uncertainty by specifying a wide range in value (Table 3); WE_{Ca} , WE_{Mg} and WE_{K} are the weathering rates of Ca, Mg and K, respectively. The Na weathering rate was set to zero and the soil and stream Na set directly from the Na vs Cl regression line.

E_{Na} , E_{Mg} , E_{Ca} and E_{K} are the fractions of the cation exchange sites occupied by Na, Mg, Ca and K in 1844. These are required to initialize the model and the ranges specified are deduced from knowledge of present-day fractions and that base cation fractions have decreased owing to acidification. The total CEC within the soil is held constant during each run.

The CO_2 partial pressure ($p\text{CO}_2$) in the soil and stream was set to 40 and 4 times the atmospheric partial pressure, respectively. The stream $p\text{CO}_2$ represents the median value calculated from the observations of bicarbonate and hydrogen and these were held constant for each run. The value of the aluminium equilibrium constant in the soil was set at 8.55. Stream Al concentrations are usually represented in MAGIC by an equilibrium with $\text{Al}(\text{OH})_3$. For the Welsh regional data, Neal et al. (1989) showed that the Al levels are better predicted by disallowing Al precipitation in the stream and this modification was used here. Soil SO_4 adsorption within the model was set from the single site analysis of Welsh catchments by Whitehead et al. (1988a) with a half saturation constant of 150 meq m^3 .

The model was run 2000 times drawing the parameters from uniform distributions whose maxima and minima are given in Table 3. The results from these runs were used in the calibration phase of the analysis. Six streamwater variables were used to calibrate the model: Ca, Mg, SO_4 , Cl, NO_3 and alkalinity. The remainder acted as free variables whose closeness of fit was used as a

TABLE 4

Bin sizes used for the final calibration procedure

Variable	Minimum ($\mu\text{eq l}^{-1}$)	Maximum ($\mu\text{eq l}^{-1}$)	Number of axis divisions
Ca	40	230	5
Mg	40	160	2
SO_4	50	300	5
Alkalinity	-250	160	5
Cl	160	400	5
NO_3	0	60	3

criterion for evaluating the model performance. The six variables were selected for their importance both in terms of their magnitude and variability in the observed data, and in terms of their influence on the biological species in the stream. The 'binning' procedure for forming the relative frequency structure for observed and simulated data entailed setting a maximum and a minimum limit for accepting simulations. The range formed on each axis was divided linearly to form the bins. The number of divisions on each axis was allowed to vary to form alternative calibration strategies. By taking many divisions the number of observations matched decreases as the bin size diminishes. By taking few divisions the model fit becomes coarse. The strategy that was accepted finally is shown in Table 4.

Calcium, SO_4 , alkalinity and Cl were each apportioned five divisions, Mg had two and NO_3 three. Increasing the number of divisions for Mg or NO_3 greatly reduced the number of observations that were able to be simulated and so a coarser fit to these variables was accepted. An alternative would have been to run the model further to see whether the gaps in the mismatch could be filled. The total number of individual bins that had one or more observations in them was 74. Of these, 19 had no matching simulation. The observations lying in these 19 bins were thus unable to be represented in the regional simulation along with the observations at the extreme unacidic end of the distributions, which were precluded by the maximum cutoffs used in forming the bins. In total 35 of the observations could not be matched. These were mostly unacidified catchments apart from the three with the lowest pH values. These three observations had relatively high alkalinities for their corresponding pH, and the model could not predict this behaviour. Mean chemistry for the observed data set was then recalculated for the remaining 95 sites (Table 5). This 'tailored' data set was then used for matching simulated and observed. In total 252 of the original 2000 simulations were accepted by the calibrated filter.

TABLE 5

Comparison of simulated and observed stream chemistry. Observed data (in parentheses) are the 'tailored' data set used for model calibration

Variable	Mean	Minimum	Maximum
pH	5.6 (5.6)	4.5 (4.2)	6.5 (6.6)
Ca	105 (106)	42 (40)	202 (208)
Mg	87 (86)	40 (44)	160 (135)
Na	206 (202)	152 (149)	295 (289)
K	14 (11)	4.6 (5.4)	38 (35)
SO_4	138 (138)	52 (49)	284 (277)
Cl	246 (244)	176 (167)	379 (365)
Alkalinity	2.8 (2.9)	- 127 (- 141)	89 (90)
Total Al	0.16 (0.18)	0.01 (0.02)	0.96 (0.67)
NO_3	25 (20)	2.3 (7.1)	60 (60)

RESULTS

The parameters that led to the 252 successful simulations are presented in Table 3 and these successful parameters span the complete range specified in the Monte Carlo analysis. A comparison of observed and simulated chemistry is presented in Table 5 where the observed data represent the 'tailored' data set used in the calibration procedure. Good fits of mean value are obtained for each of the four variables that were assigned five axis divisions in the calibration procedure (Ca, SO₄, alkalinity and Cl). A good fit is also achieved for Mg despite only allowing for two divisions in the calibration phase. The closeness of the fit to the remaining variables is very good considering that they were set as free variables and did not take part in the calibration procedure (excepting NO₃).

Table 6 presents the observed and simulated correlation structure of the joint distributions. The table shows a close fit for most correlations, with the majority of simulated correlations being within 0.1 and most of the remainder within 0.2. The worst overall fit is for K, which was not used in the calibration procedure; this is not surprising given the potential biological controls not incorporated into the MAGIC model. The mean value of K (14 µeq l⁻¹) is small

TABLE 6

Stream chemistry correlation matrices for simulated data and observed data

	Cl	SO ₄	Na	K	Mg	Ca	pH	Total Al	Alk	NO ₃
<i>Simulated data</i>										
Cl		0.2	1.0	0.1	0.3	0.3	-0.1	0.1	-0.1	0.3
SO ₄	0.2		0.3	0.2	0.4	0.5	-0.2	0.3	-0.2	0.1
Na	1.0	0.3		0.1	0.3	0.3	-0.1	0.1	0.0	0.3
K	0.3	0.2	0.1		0.0	0.0	-0.2	0.0	-0.1	0.0
Mg	0.3	0.4	0.3	0.0		0.5	0.5	-0.5	0.5	0.1
Ca	0.3	0.5	0.3	0.0	0.5		0.6	-0.4	0.6	0.3
pH	-0.1	-0.2	-0.1	-0.2	0.5	0.6		-0.8	0.1	-0.1
Total Al	0.1	0.3	0.1	0.0	-0.5	-0.4	-0.8		-0.9	0.2
Alkalinity	-0.1	-0.2	0.0	-0.1	0.5	0.6	1.0	-0.9		-0.2
NO ₃	0.3	0.1	0.3	0.0	0.1	0.3	-0.1	0.2	-0.2	
<i>Observed data</i>										
Cl		0.3	0.9	0.1	0.3	0.4	-0.1	0.1	-0.2	0.3
SO ₄	0.3		0.3	0.2	0.5	0.5	-0.2	0.1	-0.3	0.3
Na	0.9	0.3		0.2	0.5	0.3	0.2	0.0	0.0	0.5
K	0.1	0.2	0.2		0.5	0.5	0.4	-0.2	0.5	0.2
Mg	0.3	0.5	0.5	0.5		0.6	0.5	-0.3	0.5	0.4
Ca	0.4	0.5	0.3	0.5	0.6		0.4	-0.3	0.4	0.5
pH	0.1	-0.2	0.2	0.4	0.5	0.4		-0.7	0.7	0.2
Total Al	0.1	0.1	0.0	-0.2	-0.3	-0.3	-0.7		-0.6	0.1
Alkalinity	-0.2	-0.3	0.0	0.5	0.5	0.4	0.7	-0.6		0.0
NO ₃	0.3	0.3	0.5	0.2	0.4	0.5	0.2	0.1	0.0	

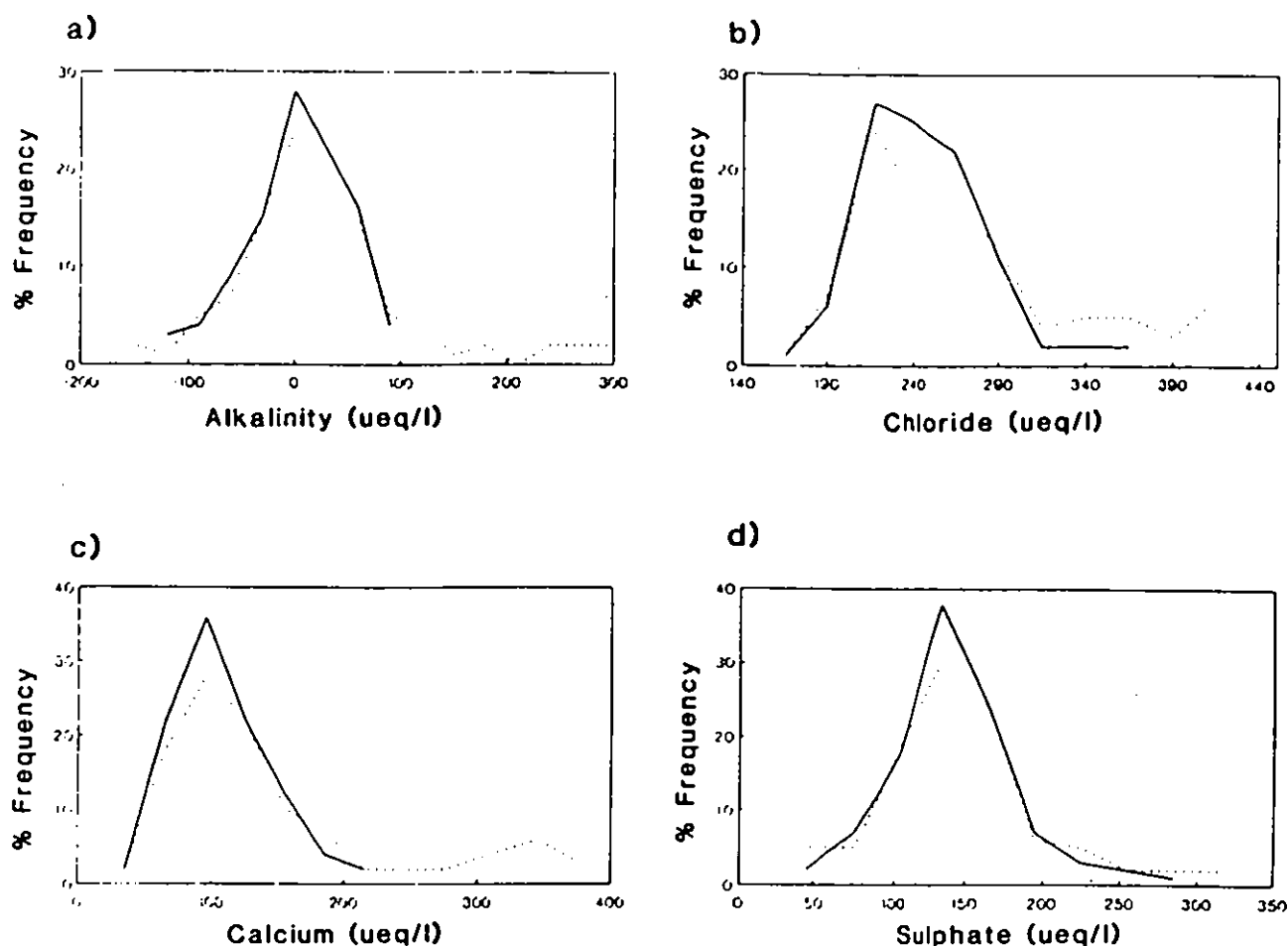


Fig. 2. Observed (---) and simulated (—) stream chemistry distributions using the full observed regional data set; (a) alkalinity, (b) chloride, (c) calcium and (d) sulphate.

compared with the other three base cations and the consequences of a poor fit to the correlation of K with the remaining variables are negligible. The very high simulated correlations for alkalinity with Al and pH reflect the strong model relationship. The fact that the observed correlations are also high indicate that these relationships are good approximations for this Welsh region.

Figure 2 shows the simulated marginal distributions for Cl, alkalinity, SO_4 and Ca compared with the distribution for the original data set containing 130 sites. Having calibrated the model to the 'tailored' data set of 95 sites, which the model was able to simulate, the match between simulated and observed is good. Although some fine structure is unable to be reproduced, the method of calibrating to a subset of the observed data is vindicated as the simulated distribution captures the general features of the water chemistry of the region.

The extent of acidification of the region since pre-industrial times can be seen by comparing the present-day stream chemistry with the stream chemistry reconstructed for 1844. From 1844 to 1984, mean pH dropped from 6.4 to 5.6; mean alkalinity has declined by an order of magnitude (from 63 to $3 \mu\text{eq l}^{-1}$), and the mean sum of acid anions ($\text{Cl} + \text{SO}_4 + \text{NO}_3$) has more than doubled (from 278 to $584 \mu\text{eq l}^{-1}$). Breaking down the pH changes reveals that 40 of the

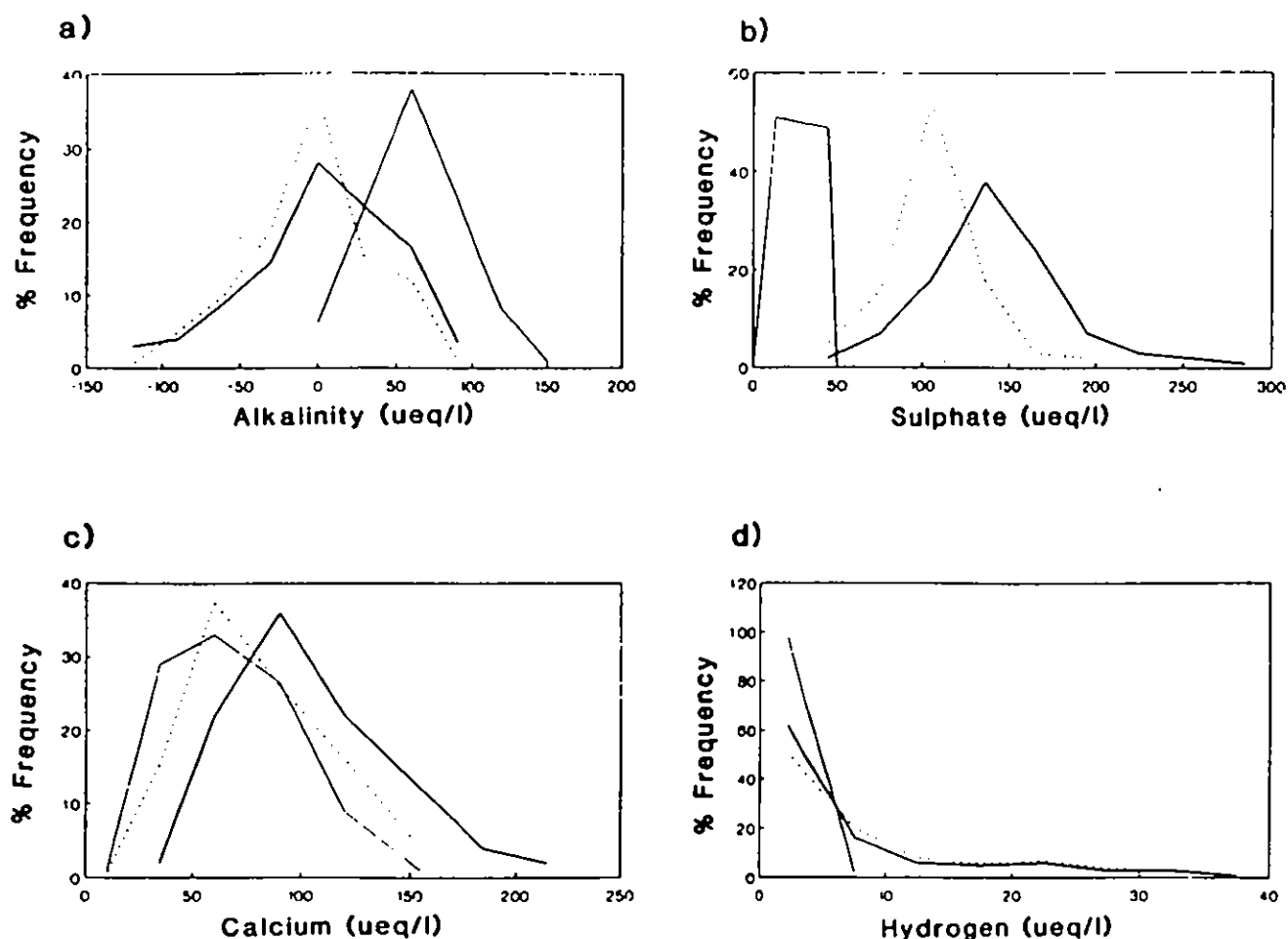


Fig. 3. Simulated background (—), present day (---) and future (---) stream chemistry assuming a 30% decrease in acid deposition; (a) alkalinity, (b) sulphate, (c) calcium and (d) hydrogen.

catchments have a simulated pH drop < 0.5 , 37 catchments show a pH drop between 0.5 and 1.5, and 18 catchments show a drop in pH > 1.5 units. The number of catchments represented in any particular chemical class is determined by summing the weights of all the simulations falling within that class. Figure 3 shows the simulated regional weighted distributions in 1844 and 1984 for alkalinity, Ca, SO_4 and hydrogen. Also shown are model predictions into the future with a pollutant deposition loading of 70% of its present-day level. Calcium shows a slight return toward the 1844 conditions whereas the hydrogen remains more or less the same. The large change in SO_4 reflects the high pollutant loading since 1844.

The accepted model parameters were fed back into the model in an attempt to assess the ability of the region to recover from acidification. Several future deposition scenarios were used: Fig. 4 shows the effect of reduction in pollutant deposition on both alkalinity and pH. A 30% reduction of pollutant deposition is required to halt acidification in Wales and reductions greater than this may start to reverse the acidification at most sites. All sites show a pH recovery of at least 0.2 under a 70% reduction scenario. Table 7 shows the results for 30%, 50% and 70% reduction of deposition reflecting scenarios that are currently

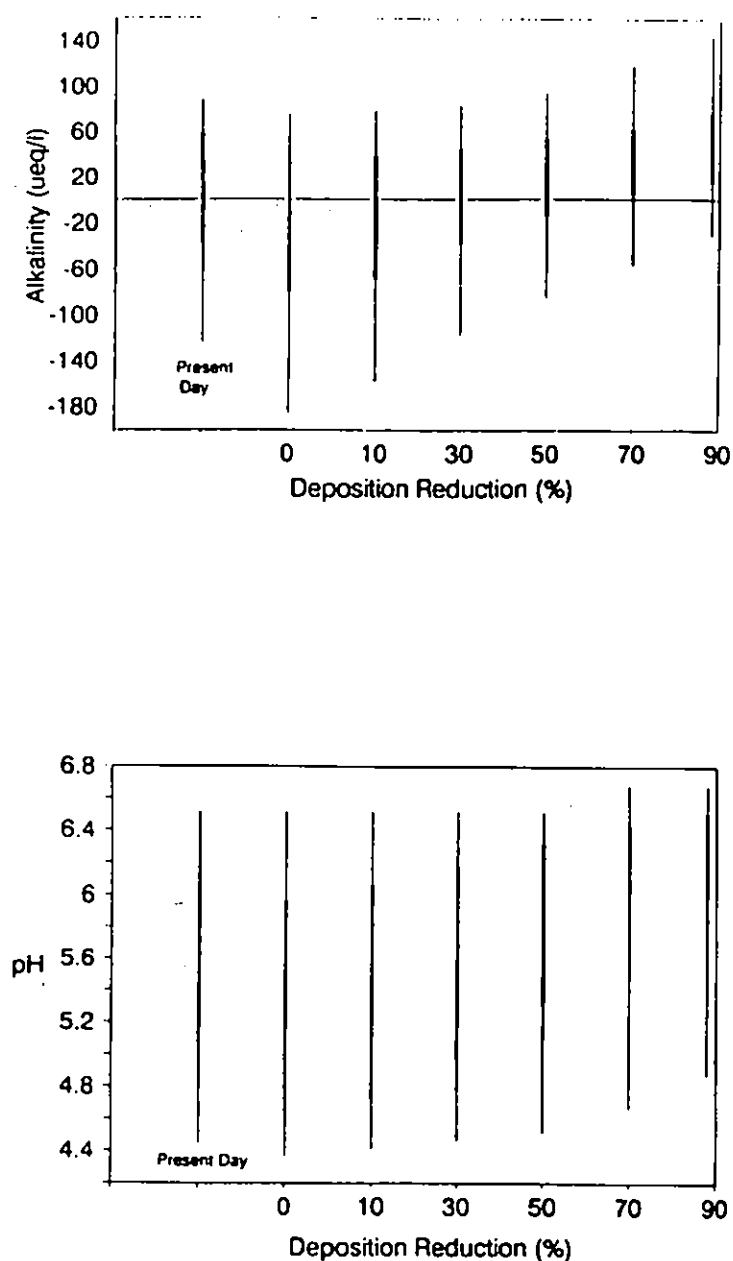


Fig. 4. Forecast stream pH and alkalinity (mean, standard deviation and extremes of the distributions) under a range of deposition reduction strategies.

believed to be achievable. Overall, by decreasing deposition of pollutants it is seen that the alkalinity and pH will rise whereas the base cation concentrations will fall. This decline in base cation concentration in the stream is the result of the decline of acid anion pollutants.

DISCUSSION AND CONCLUSIONS

A regional model of a part of Wales, believed to be sensitive to acid deposition, has been presented. The model has been used to predict the extent of acidification through the region and has enabled a dose-effect type of relationship, for reducing the deposition of acid pollutants, to be predicted. The model has been tested successfully against present-day joint distributions of

TABLE 7

Predicted stream chemistry under 70%, 50% and 30% deposition reduction strategies

	Mean	Standard deviation	Minimum	Maximum
<i>70% deposition reduction</i>				
pH	6.0	0.3	4.7	6.9
Ca	72.1	17.7	14.3	150.8
Mg	64.6	7.8	39.6	99.8
Na	201.7	16.0	152.6	293.5
SO ₄	62.6	7.4	33.9	105.1
Cl	246.4	23.0	175.8	379.3
Alk	28.8	18.7	-60.2	118.2
Al	0.06	0.03	0.006	0.41
<i>50% deposition reduction</i>				
pH	5.7	0.3	4.5	6.5
Ca	77.1	18.0	16.8	151.6
Mg	67.7	8.3	40.2	102.2
Na	202.6	16.0	152.8	293.8
SO ₄	83.8	11.4	38.8	155.7
Cl	246.4	23.0	175.8	379.2
Alk	12.3	20.9	-92.3	92.9
Al	0.09	0.06	0.009	0.63
<i>30% deposition reduction</i>				
pH	5.4	0.4	4.5	6.5
Ca	80.7	18.8	17.1	154.3
Mg	69.6	9.1	40.2	117.6
Na	203.2	16.0	152.8	294.2
SO ₄	104.8	15.5	43.7	203.6
Cl	246.4	23.0	175.8	379.2
Alk	-6.8	25.7	-125.7	82.3
Al	0.17	0.10	0.01	0.90

All units in $\mu\text{eq l}^{-1}$, except pH and Al (mg l^{-1}).

water chemistry. The simulated range of pH decline across the region is compatible with that reported by Battarbee et al. (1988), who looked at the evidence for acidification of several lakes, in the same study region, using diatom analysis.

Assuming the catchments across the region to be broadly similar in response to acidification, the present-day chemistry may represent the response of any one site through time, i.e. all of the catchments will be at a different stage of acidification. Some were poorly buffered from the start and will be highly acidified whereas others will have been buffered to a greater extent. Collectively they may allow a substitution of space for time in the interpretation of the sampling variable. If this is the case then predictions using the same relationships may be assumed to be reasonable. Another indirect way of testing the

model is to use the predictions to feed biological models of fish density, survival and floral and macroinvertebrate speciation (Ormerod et al., 1988). The results of this two-stage modelling may be compared with biological evidence for trends in acidification. Of crucial importance to these biological models is the stream Al concentration and its time trend. The submodel used here allows no net Al precipitation in the stream on a mean annual basis. Other hypotheses that could have been used include: (1) allowing precipitation only when saturation of Al occurs in the stream; (2) having a different phase of Al in each site; (3) having a depletable finite store of Al encompassing a range of solubilities in the pristine state so that as the catchment acidifies the more soluble phases are flushed from the soil; (4) ion exchange of Al in the soil, with a finite store; (5) using a two box version of MAGIC, with a mixing box at soil CO₂ partial pressure before release into the stream; (6) fitting an empirical curve to the data which is assumed constant through time. Each of the alternatives needs to be examined before concrete Al predictions may be made.

The timing of acidification in the region has not been presented because the key to the time trend is the deposition sequence of pollutants since 1844. The model uses emission data for the U.K. to predict the trend in deposition. This may not accurately represent the actual deposition trend for Wales. Further evidence is required and this may come from the record of historical deposition of carbonaceous soot particles in lakes. The model has been used to indicate possible future trends for acidification in Welsh catchments under a number of deposition reduction strategies. To see how these relate to reductions in emissions, a model of atmospheric pollutant transport must be applied across the region.

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APPENDIX B

Comparison of Water Chemistry Distributions for Each Scenario in 2034

Figure B1. Alkalinity

Figure B2. Aluminium

Figure B3. Hydrogen

Figure B4. Sulphate

Figure B5. Calcium

Figure B6. Magnesium

Figure B7. Sodium

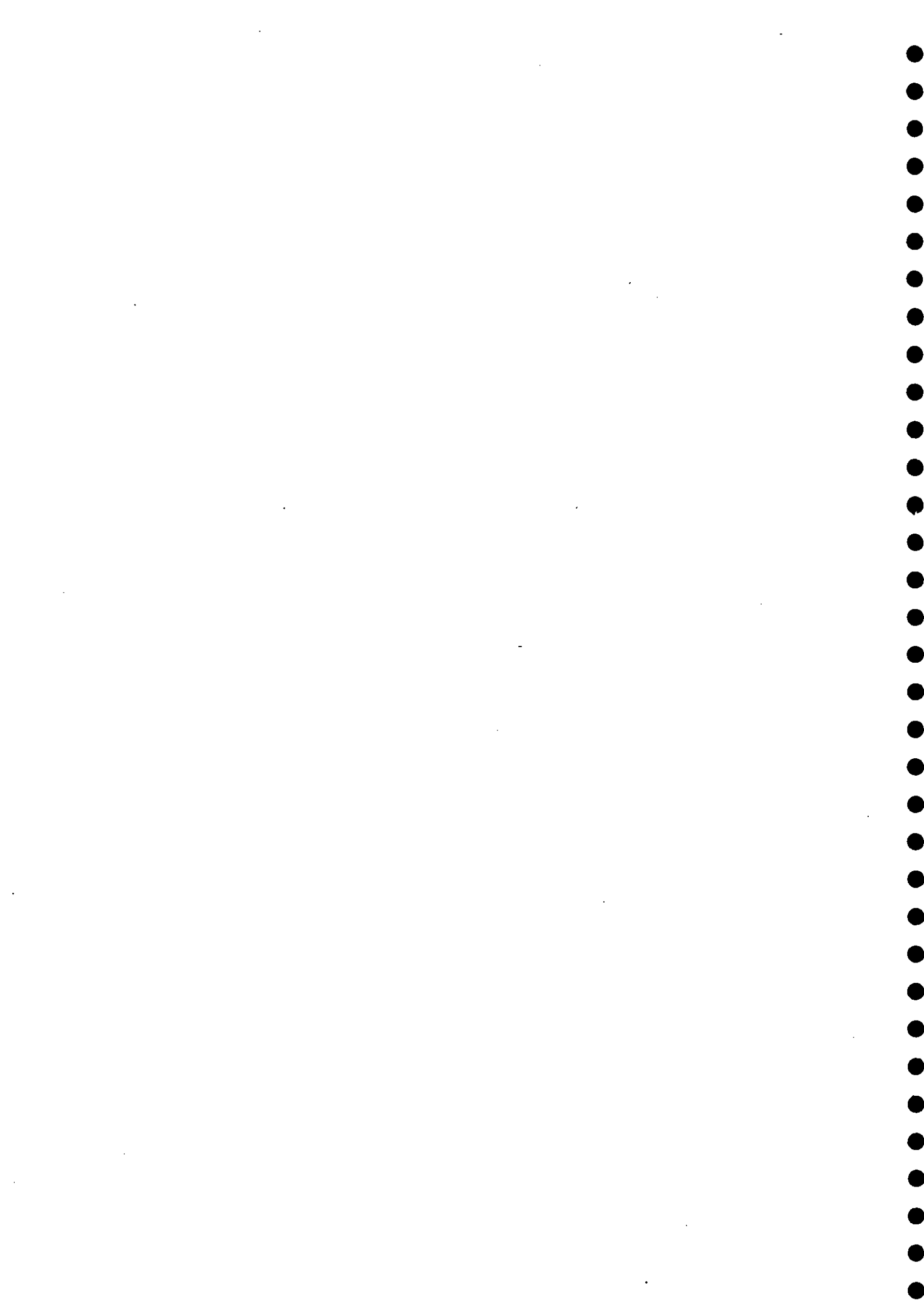


Figure B1

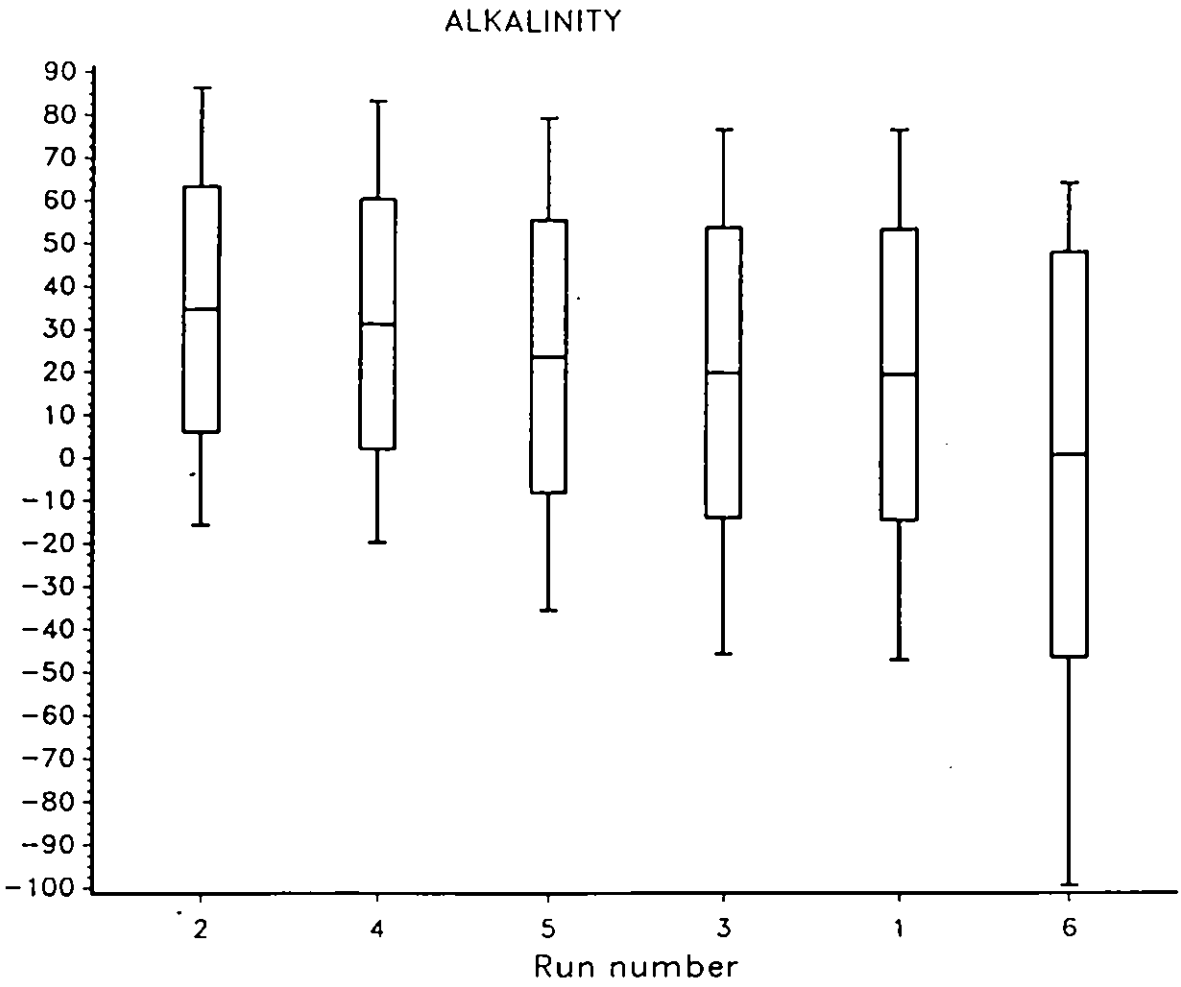
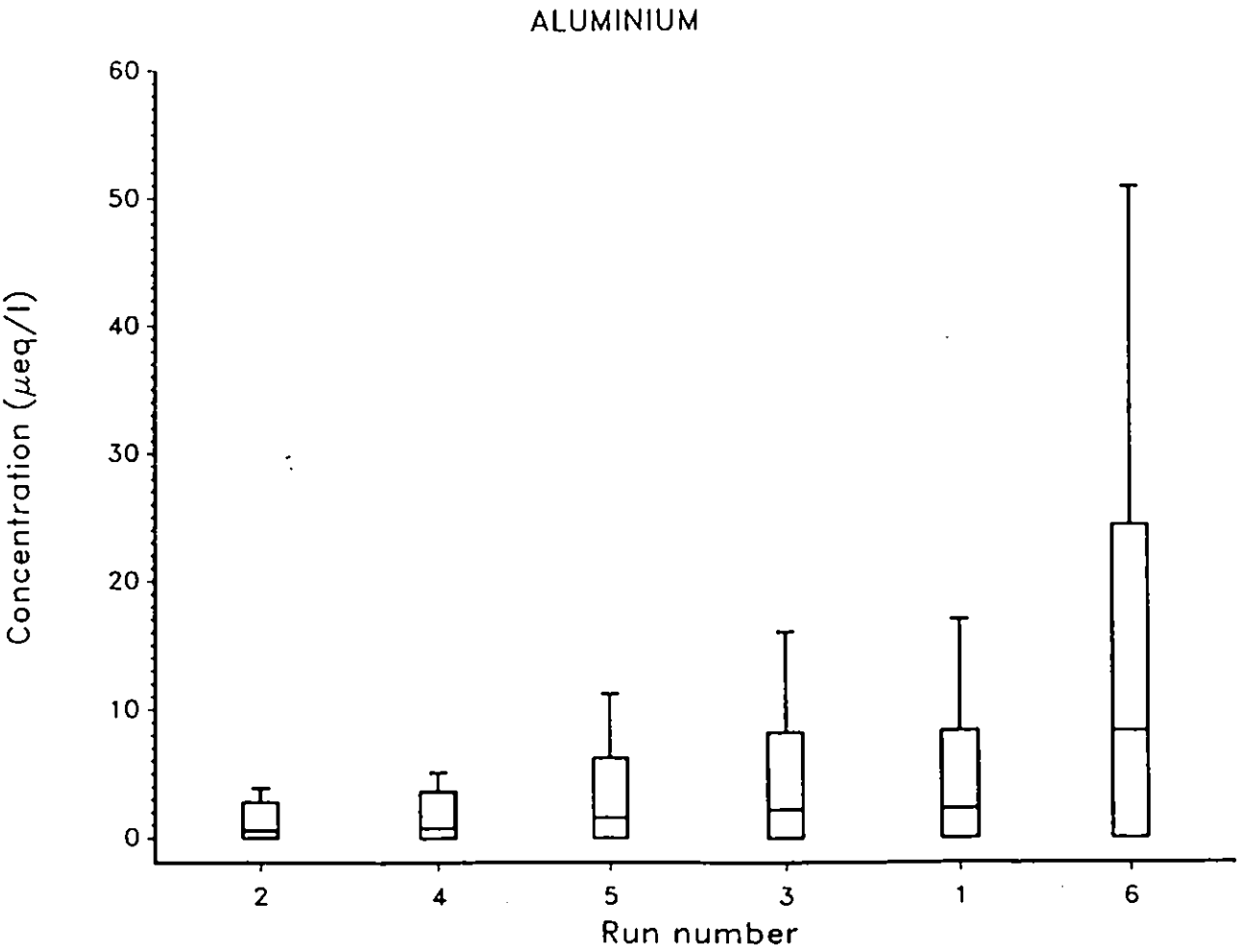
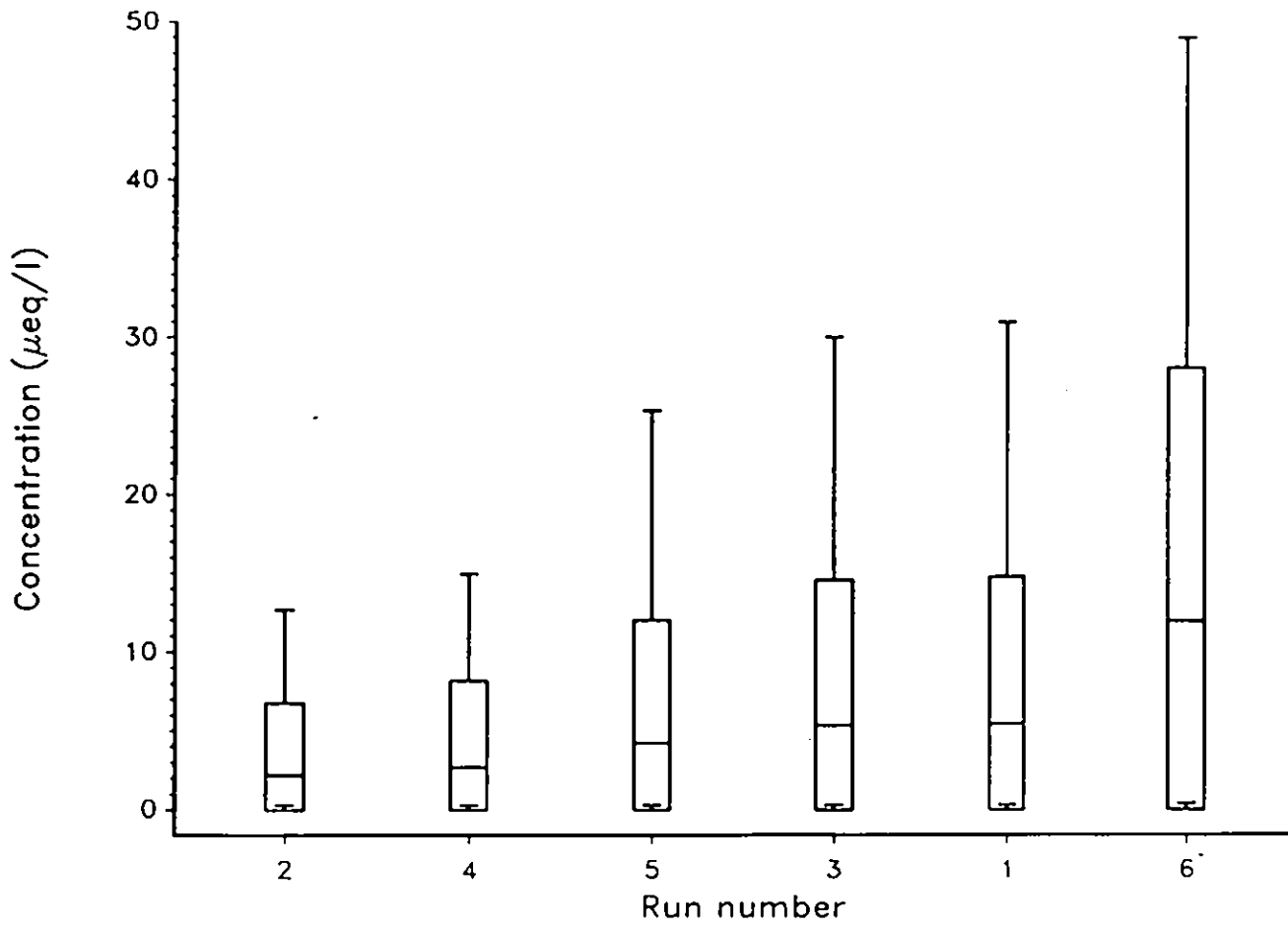


Figure B2



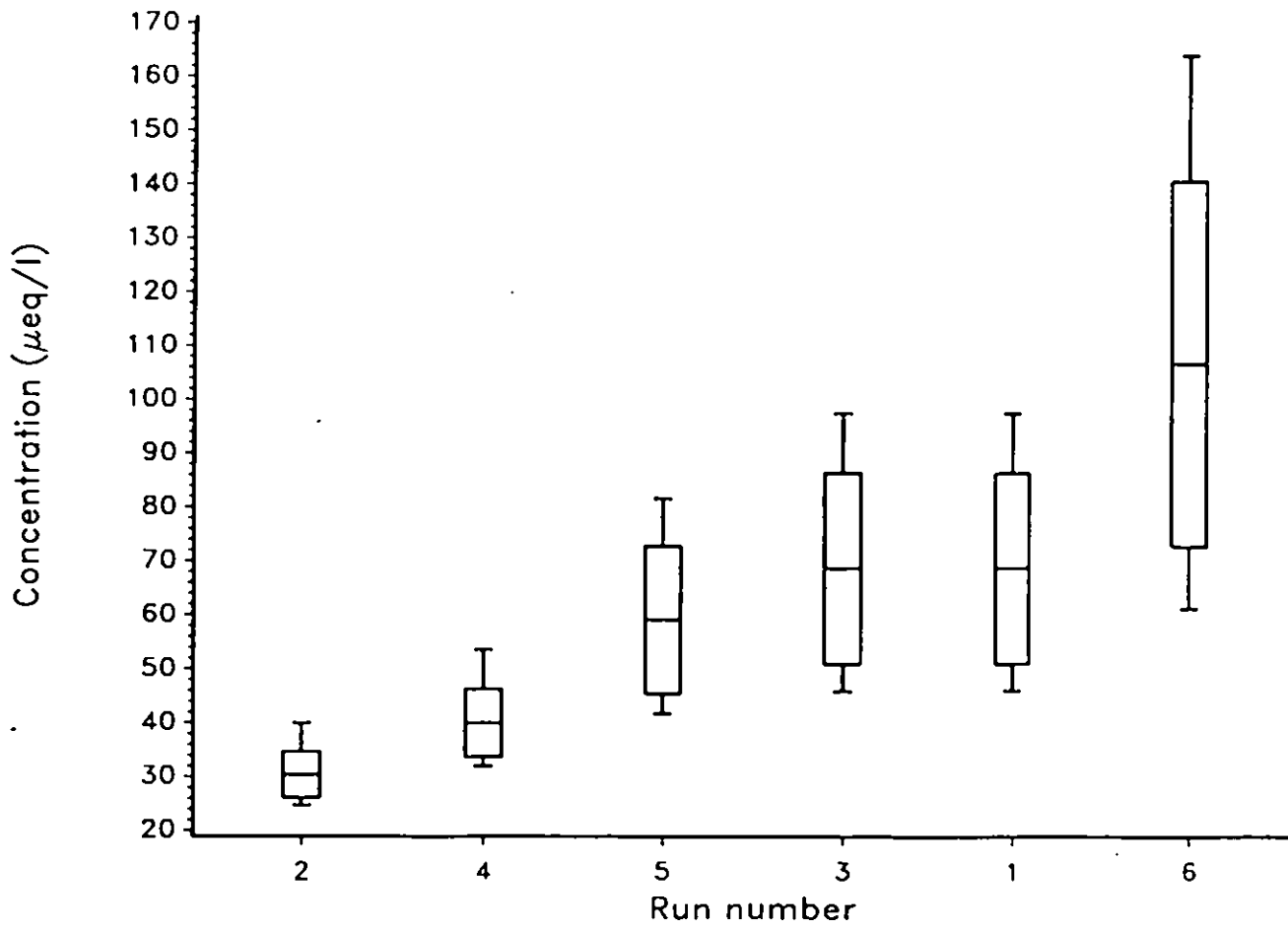
HYDROGEN

Figure B3



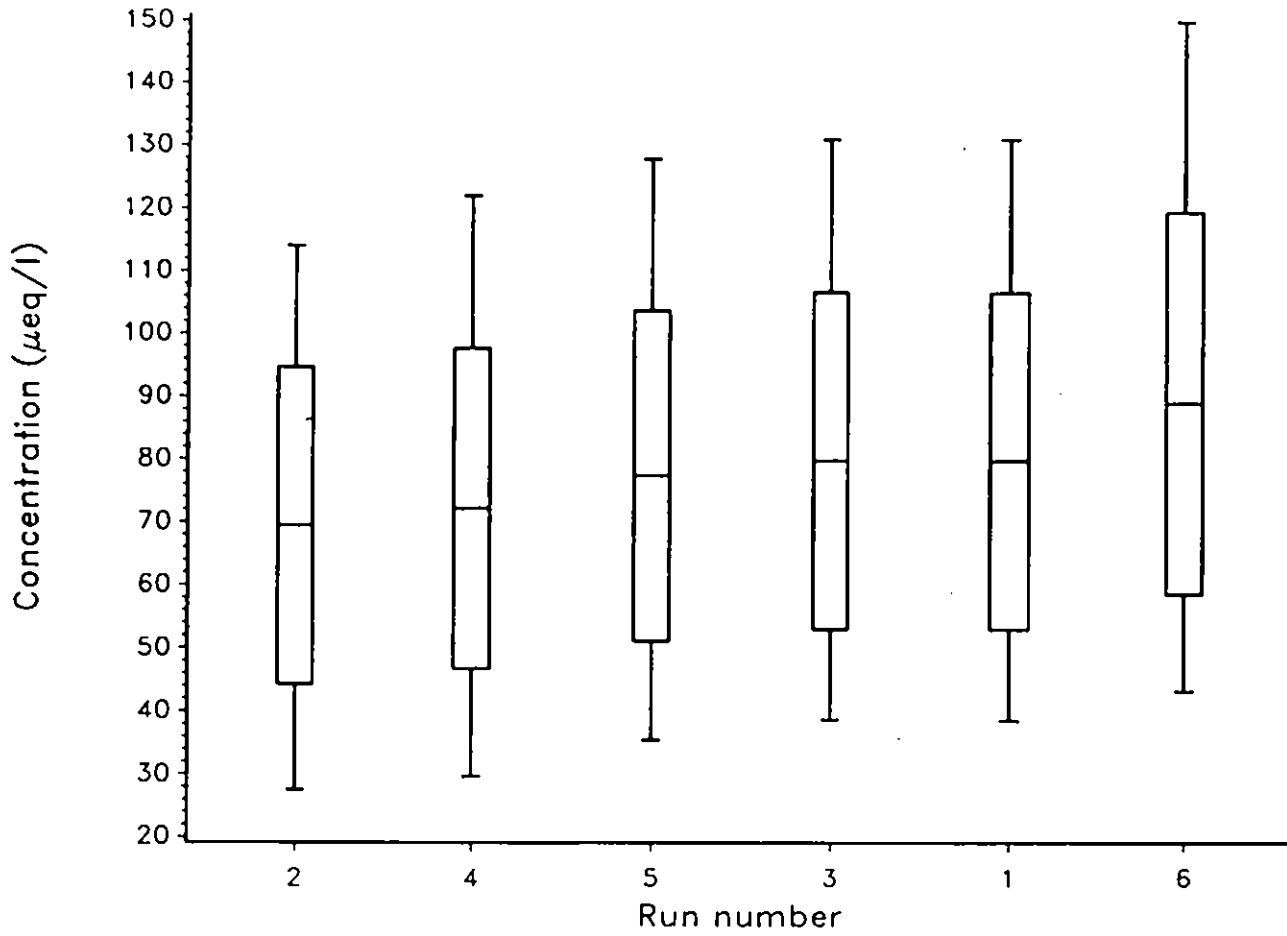
SULPHATE

Figure B4



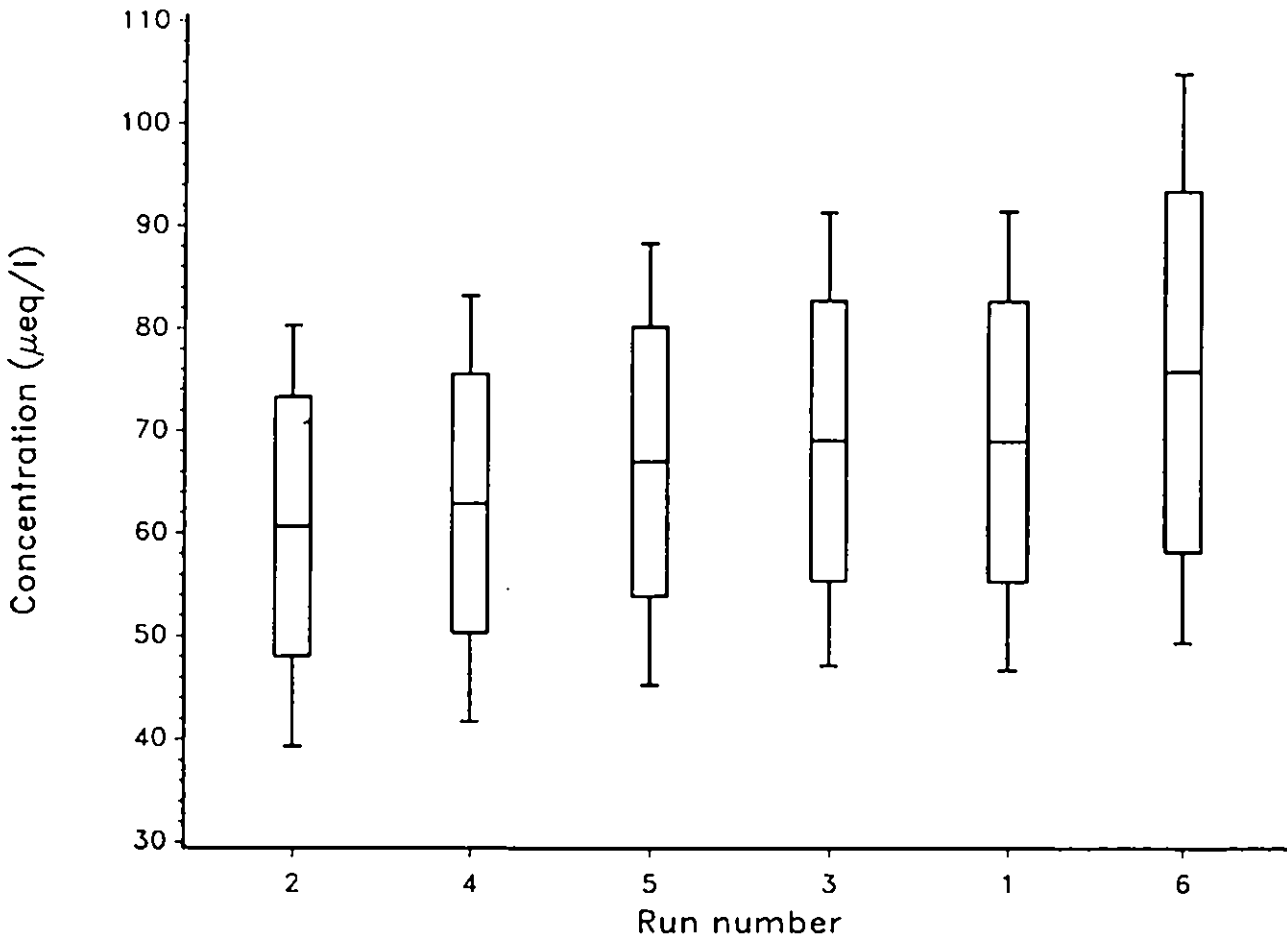
CALCIUM

Figure B5



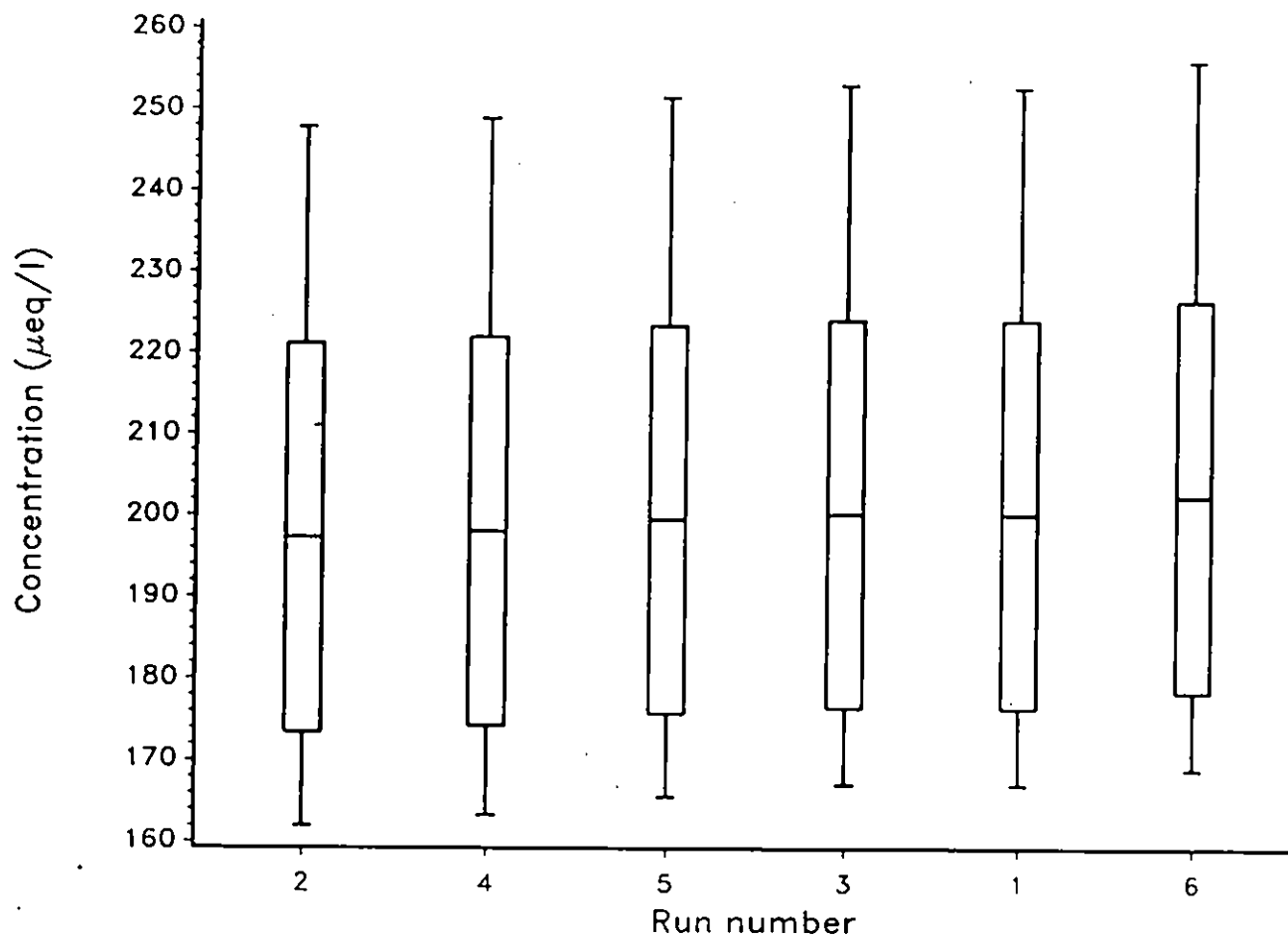
MAGNESIUM

Figure B6



SODIUM

Figure B7



APPENDIX C

Summary Statistics of Predicted Ion Distributions in 2034 For Each Deposition Reduction Scenario

Table C1. Hydrogen

Table C2. Alkalinity

Table C3. Aluminium

Table C4. Sodium

Table C5. Calcium

Table C6. Magnesium

Table C7. Chloride

Table C8. Sulphate

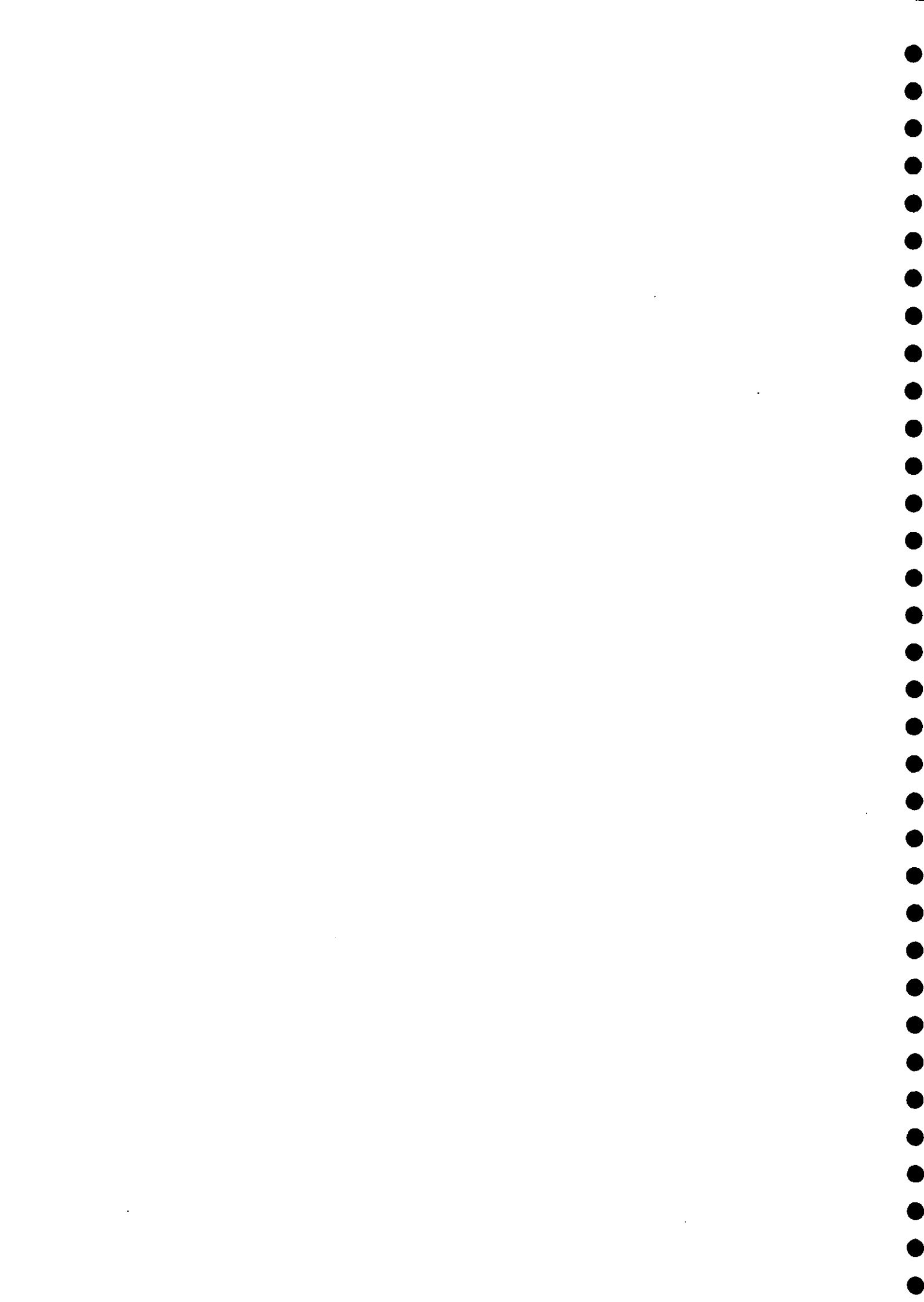


Table C1 Predicted distribution of hydrogen for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	5.43	2.21	5.35	2.71	4.23	11.90
Standard Deviation:	9.27	4.57	9.19	5.49	7.77	16.02
Variance:	85.97	20.89	84.55	30.14	60.36	256.77
5 Percentile:	0.30	0.30	0.30	0.30	0.30	0.40
95 Percentile:	30.91	12.70	29.95	14.98	25.31	48.89
Maximum:	46.50	36.10	46.50	39.10	43.90	57.00
Minimum:	0.30	0.20	0.30	0.20	0.30	0.30

Table C2 Predicted distribution of alkalinity for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	19.15	34.62	19.54	31.12	23.54	0.61
Standard Deviation:	33.87	28.63	33.79	29.18	31.73	47.22
Variance:	1147.0	819.41	1142.2	851.26	1007.0	2229.6
5 Percentile:	-47.28	-15.73	-45.98	-19.88	-35.51	-99.52
95 Percentile:	76.06	86.28	76.08	83.22	79.07	63.92
Maximum:	91.2	111.10	92.30	104.90	95.80	83.00
Minimum:	-91.00	-59.40	-91.00	-67.50	-82.10	-135.30

Table C3 Predicted distribution of aluminium for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	2.27	0.56	2.22	0.78	1.55	8.29
Standard Deviation:	6.07	2.24	6.00	2.87	4.65	16.01
Variance:	36.83	5.02	36.05	8.23	21.64	256.43
5 Percentile:	0.00	0.00	0.00	0.00	0.00	0.00
95 Percentile:	17.02	3.89	16.04	5.12	11.21	50.86
Maximum:	46.00	24.6	46.00	29.60	39.5	80.10
Minimum:	0.00	0.00	0.00	0.00	0.00	0.00

Table C4 Predicted distribution of sodium for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	200.17	197.32	200.29	198.13	199.58	202.39
Standard Deviation:	23.75	23.84	23.76	23.79	23.75	23.95
Variance:	564.26	568.49	564.72	566.13	564.19	573.49
5 Percentile:	167.10	162.05	167.15	163.35	165.65	169.00
95 Percentile:	252.40	247.80	252.75	248.69	251.19	255.69
Maximum:	293.40	291.90	293.40	292.70	293.20	294.40
Minimum:	152.30	150.90	152.50	151.40	152.20	152.80

Table C5 Predicted distribution of calcium for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	79.71	69.49	79.82	72.17	77.32	88.93
Standard Deviation:	26.80	25.21	26.81	25.46	26.26	30.42
Variance:	718.34	635.44	718.81	648.43	689.59	925.09
5 Percentile:	38.48	27.52	38.59	29.67	35.39	43.07
95 Percentile:	130.95	114.08	130.96	121.95	127.68	149.65
Maximum:	150.50	145.70	150.80	146.90	148.60	171.30
Minimum:	19.80	11.80	19.80	13.90	17.90	26.60

Table C6 Predicted distribution of magnesium for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	68.97	60.76	69.09	62.99	67.13	75.78
Standard Deviation:	13.69	12.62	13.68	12.60	13.13	17.59
Variance:	187.64	159.21	187.15	158.87	172.43	309.32
5 Percentile:	46.69	39.35	47.21	41.78	45.33	49.38
95 Percentile:	91.46	80.34	91.38	83.24	88.40	104.88
Maximum:	106.10	98.90	106.00	99.10	100.40	130.00
Minimum:	39.10	34.00	39.20	35.50	38.10	40.20

Table C7 Predicted distribution of chloride for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	243.70	243.70	243.70	243.70	243.70	243.70
Standard Deviation:	33.96	33.96	33.96	33.96	33.96	33.96
Variance:	1153.4	1153.4	1153.4	1153.4	1153.4	1153.4
5 Percentile:	198.33	198.33	198.33	198.33	198.33	198.33
95 Percentile:	319.69	319.69	319.69	319.69	319.69	319.69
Maximum:	379.20	379.20	379.20	379.20	379.20	379.20
Minimum:	175.80	175.80	175.80	175.80	175.80	175.80

Table C8 Predicted distribution of sulphate for 2034 under different deposition reduction scenarios.

	Run Number					
	1	2	3	4	5	6
Mean:	68.63	30.41	68.63	39.97	59.09	106.66
Standard Deviation:	17.70	4.24	17.70	6.28	13.69	33.94
Variance:	313.45	17.94	313.46	39.38	187.43	1151.8
5 Percentile:	45.92	24.72	45.92	31.96	41.77	61.19
95 Percentile:	97.51	39.89	97.51	53.60	81.57	164.15
Maximum:	130.50	47.30	130.50	58.30	105.10	231.70
Minimum:	36.40	21.90	36.40	28.50	33.90	46.10



APPENDIX D

Simulated 1984 and 2034 Percent Frequency Distributions For Each Scenario

Figure D1(a - g). RUN 1

Figure D2(a - g). RUN 2

Figure D3(a - g). RUN 3

Figure D4(a - g). RUN 4

Figure D5(a - g). RUN 5

Figure D6(a - g). RUN 6

Figure Dn(a) = Alkalinity

(b) = Aluminium

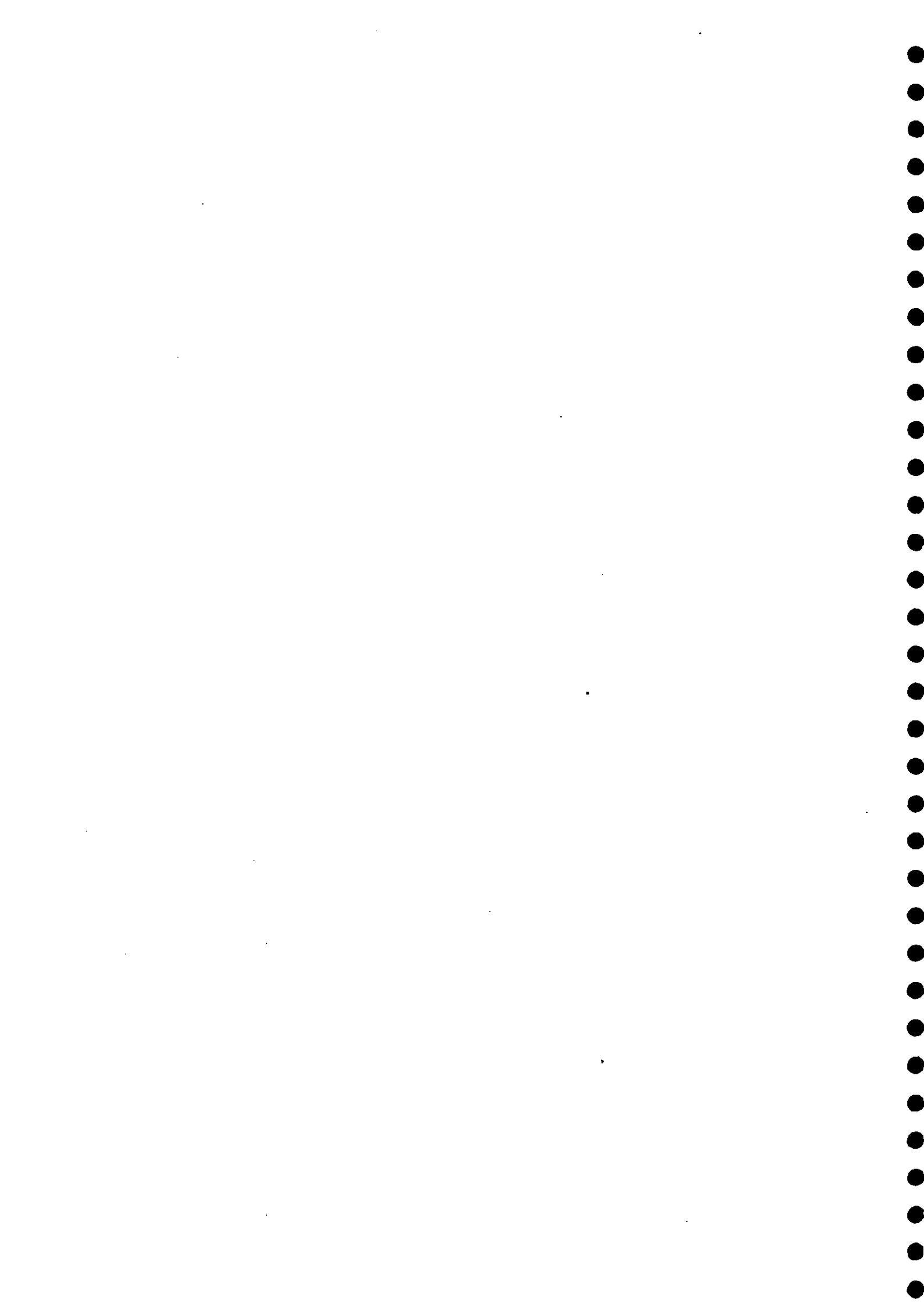
(c) = Hydrogen

(d) = Sulphate

(e) = Calcium

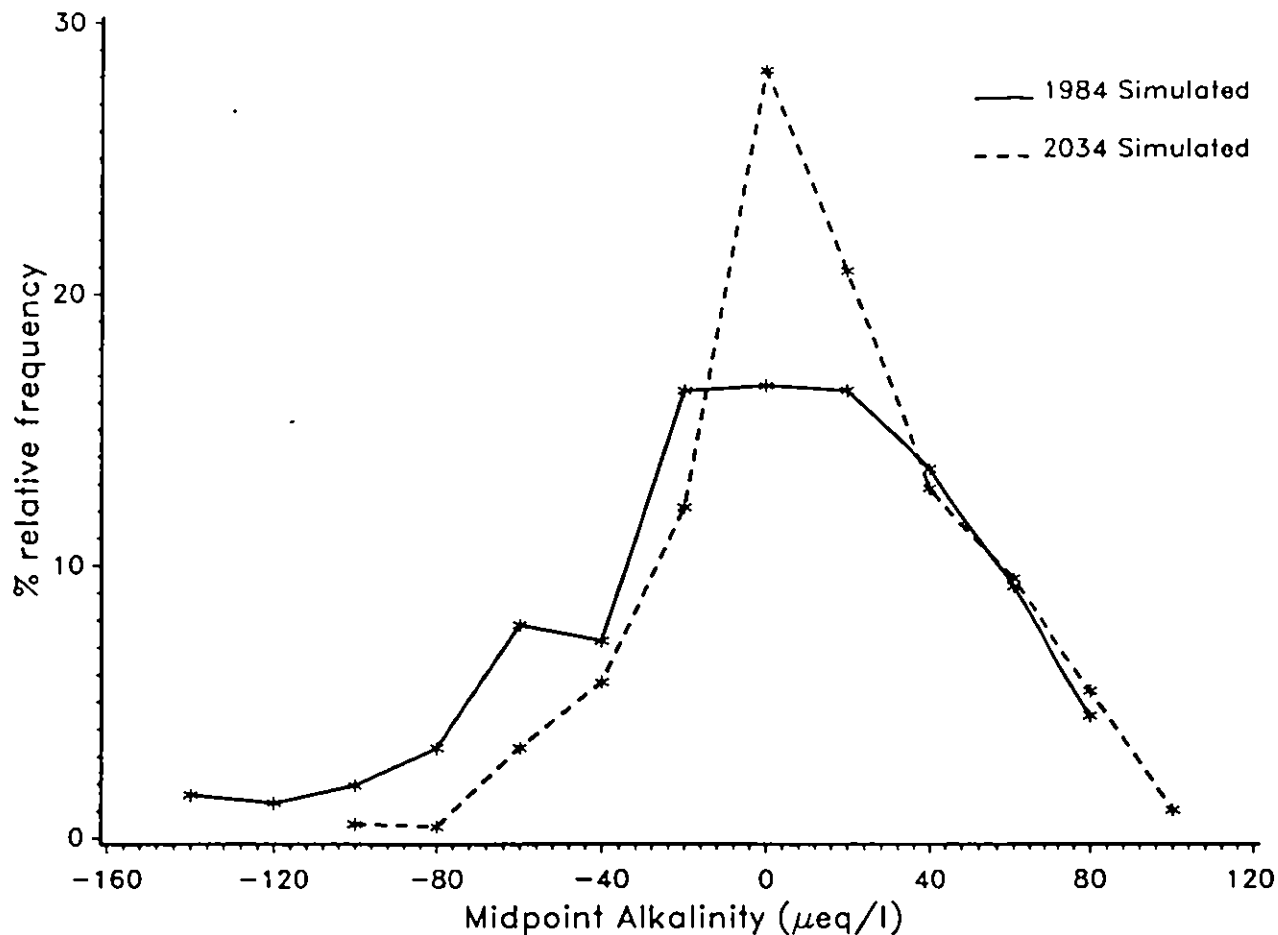
(f) = Magnesium

(g) = Sodium



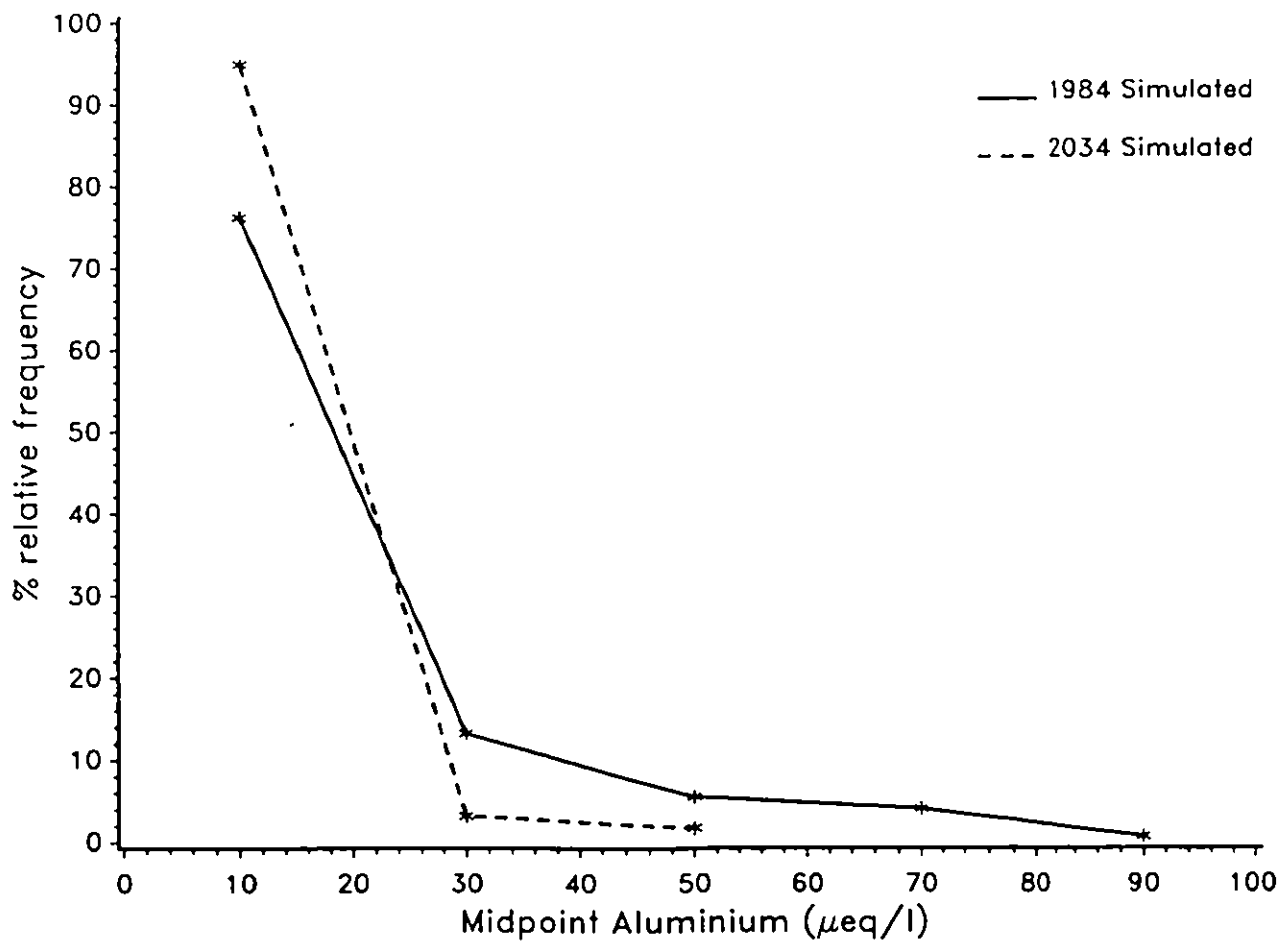
ALKALINITY

Figure D1 (a)



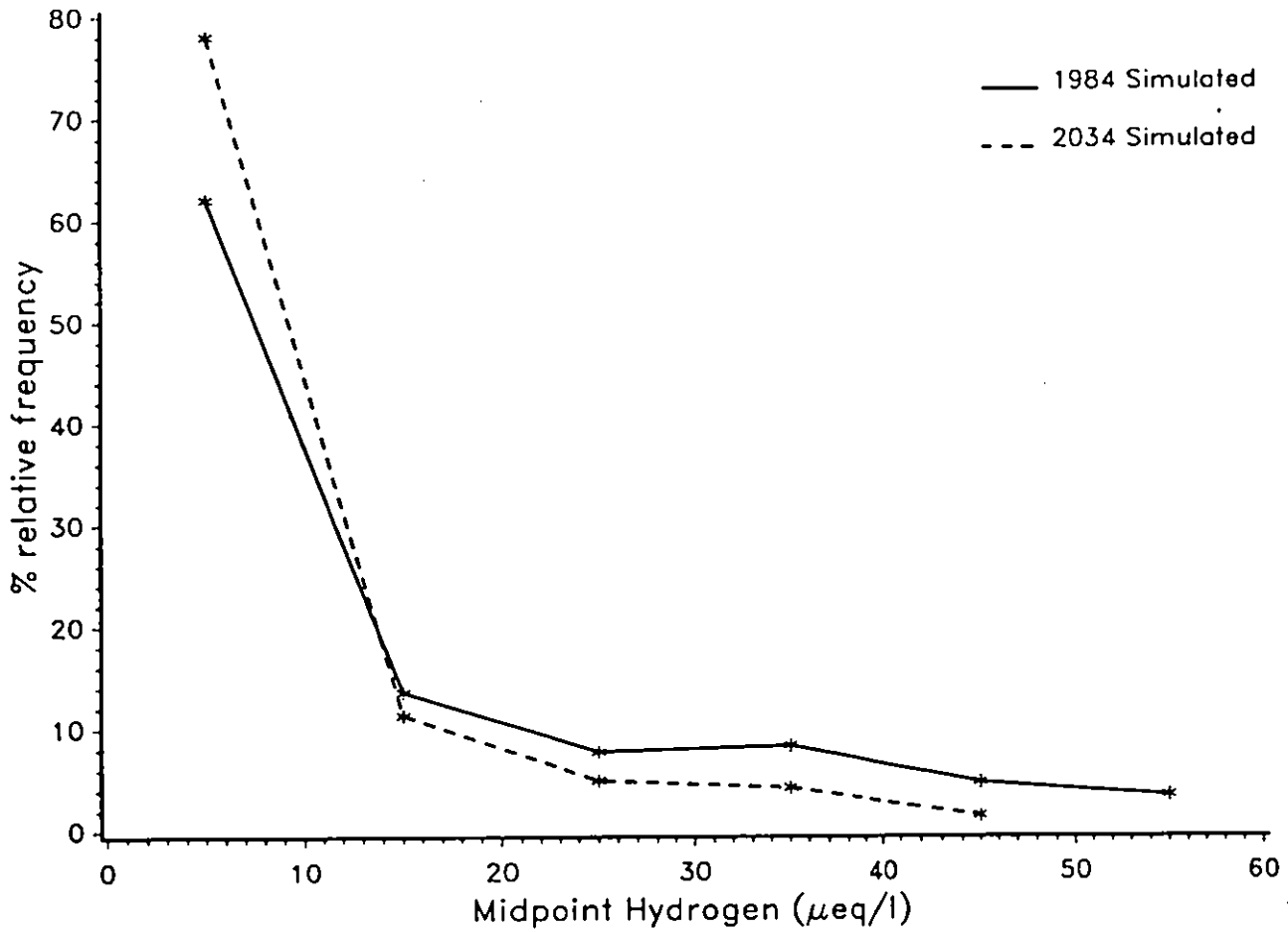
ALUMINIUM

Figure D1 (b)



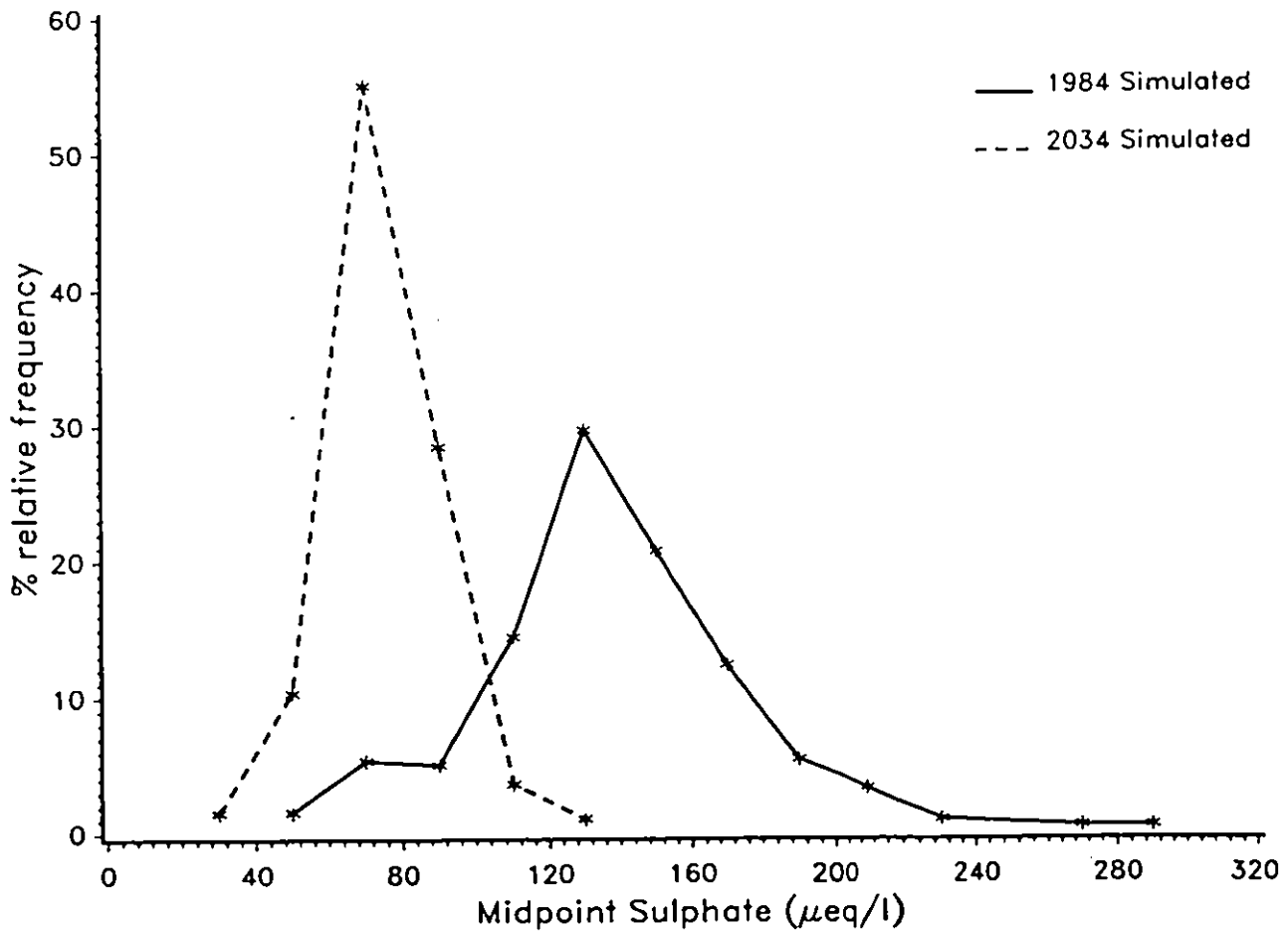
HYDROGEN

Figure D1 (c)



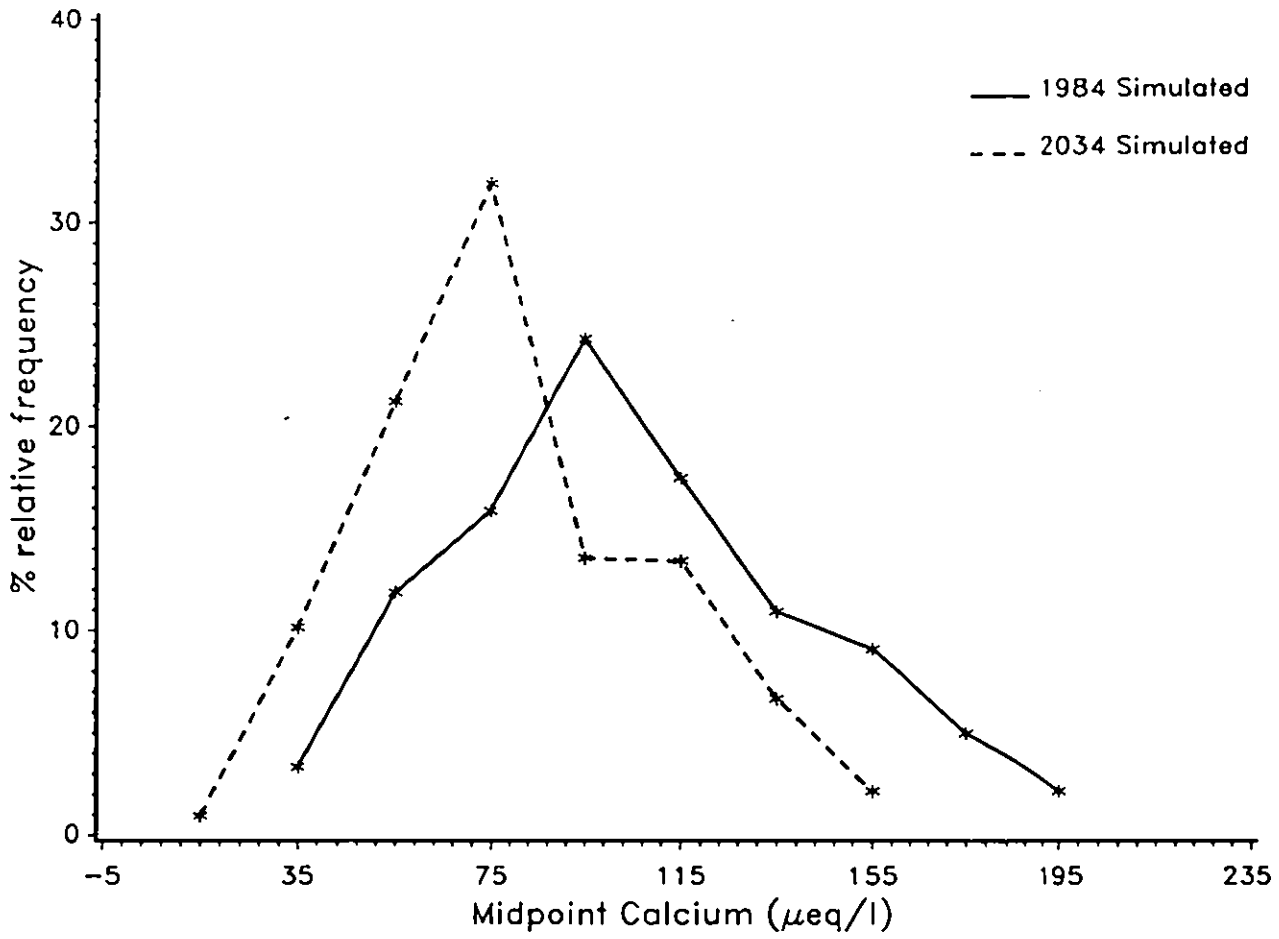
SULPHATE

Figure D1 (d)



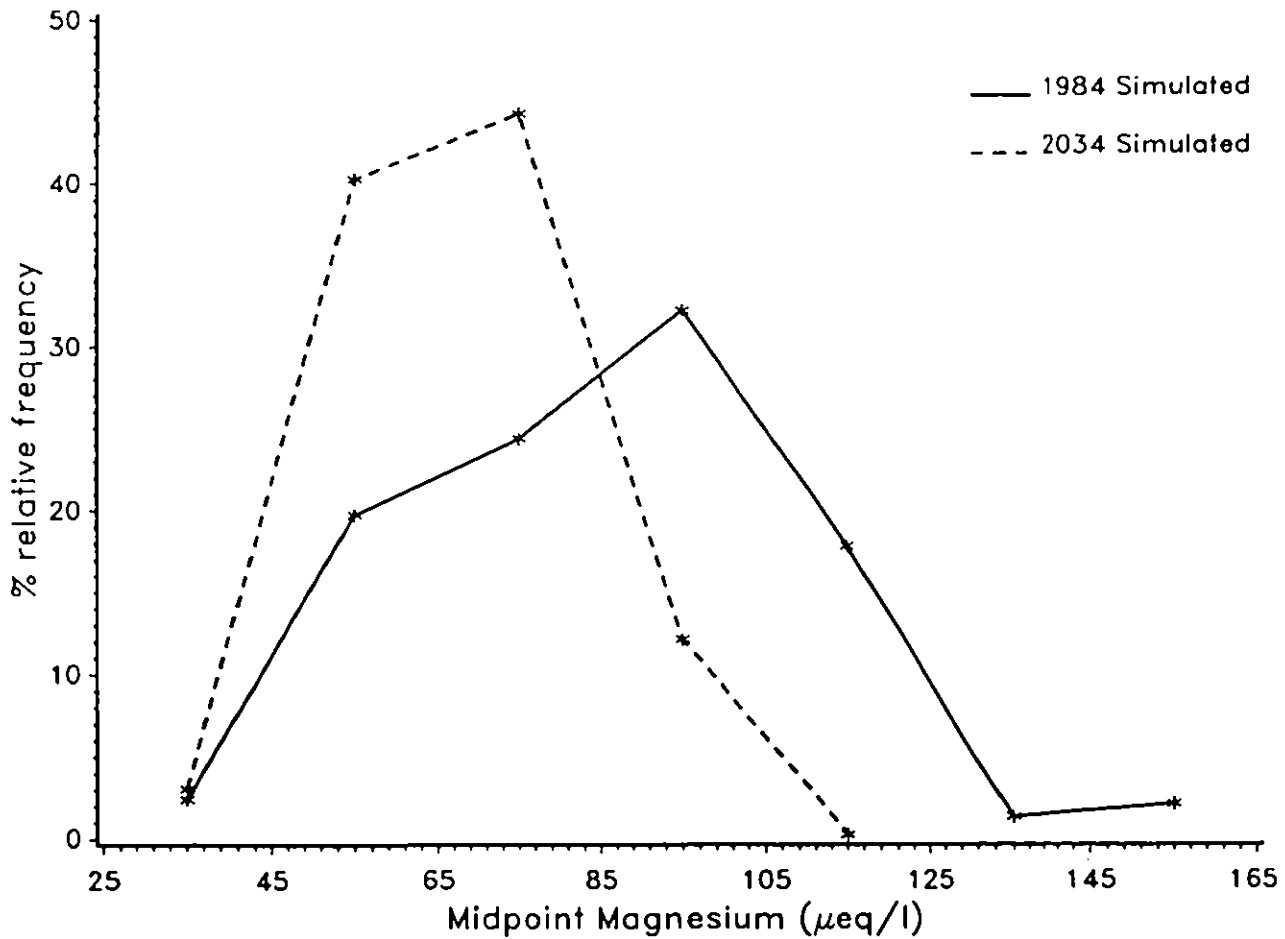
CALCIUM

Figure D1 (e)



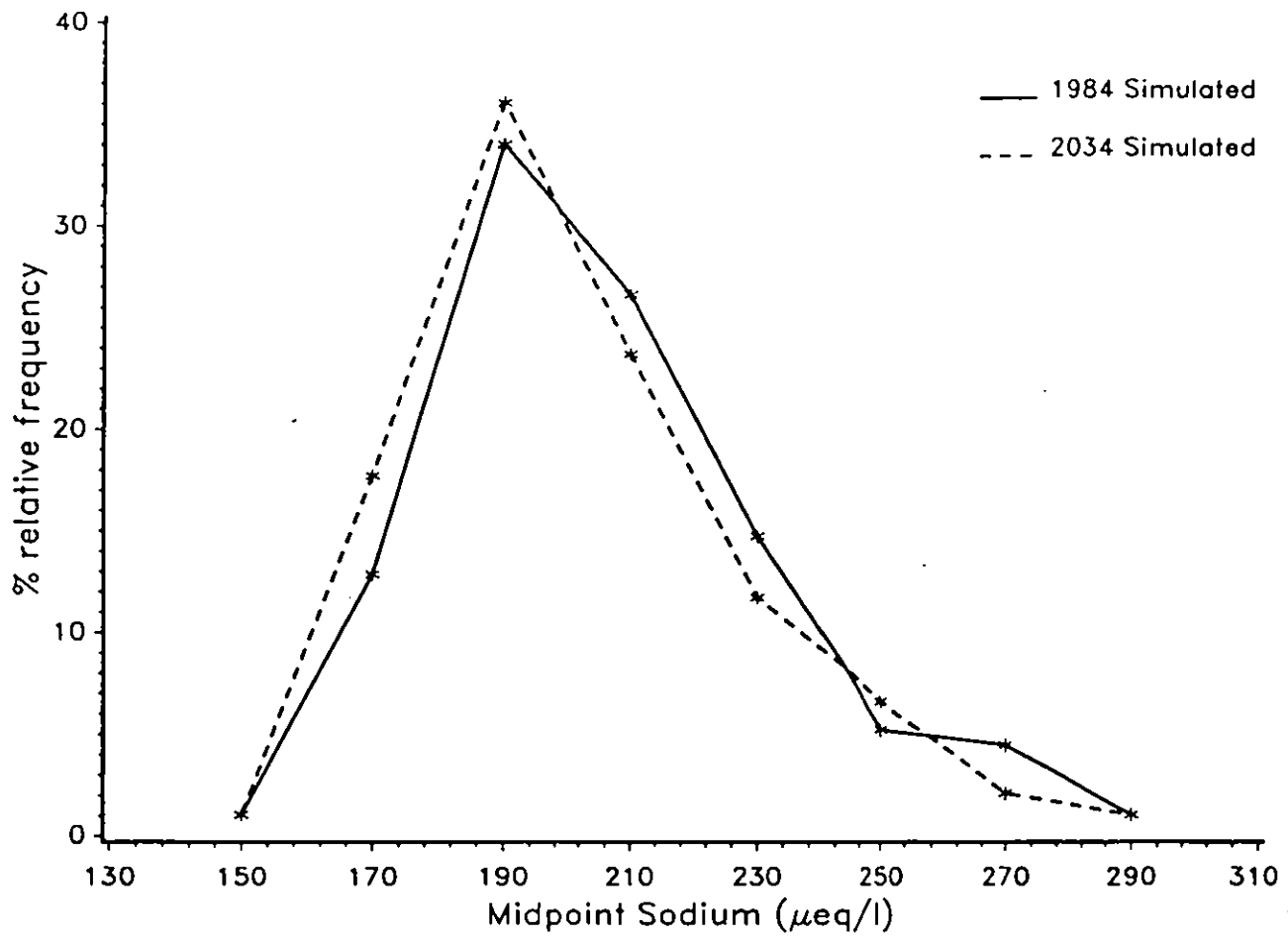
MAGNESIUM

Figure D1 (f)



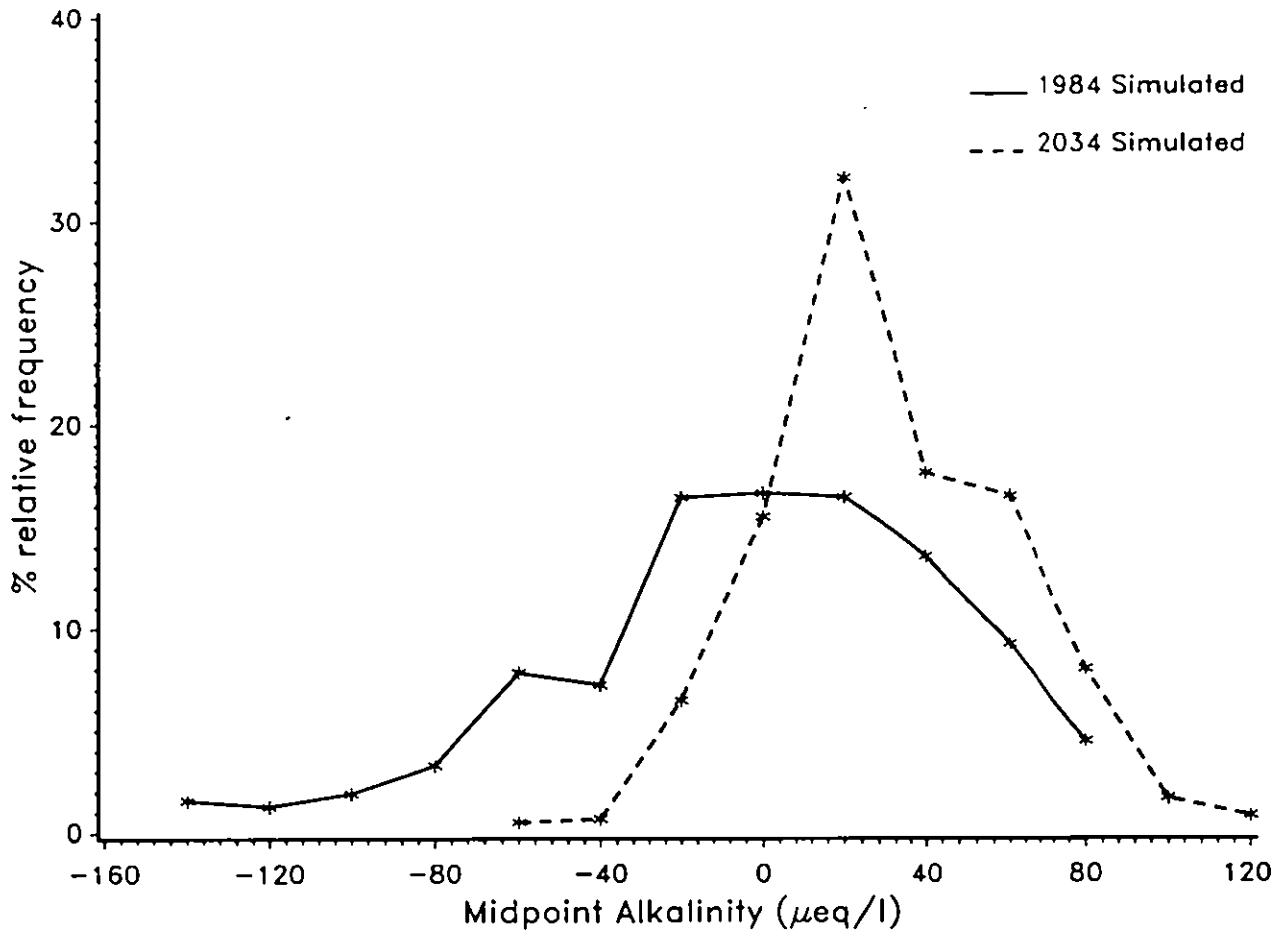
SODIUM

Figure D1 (g)



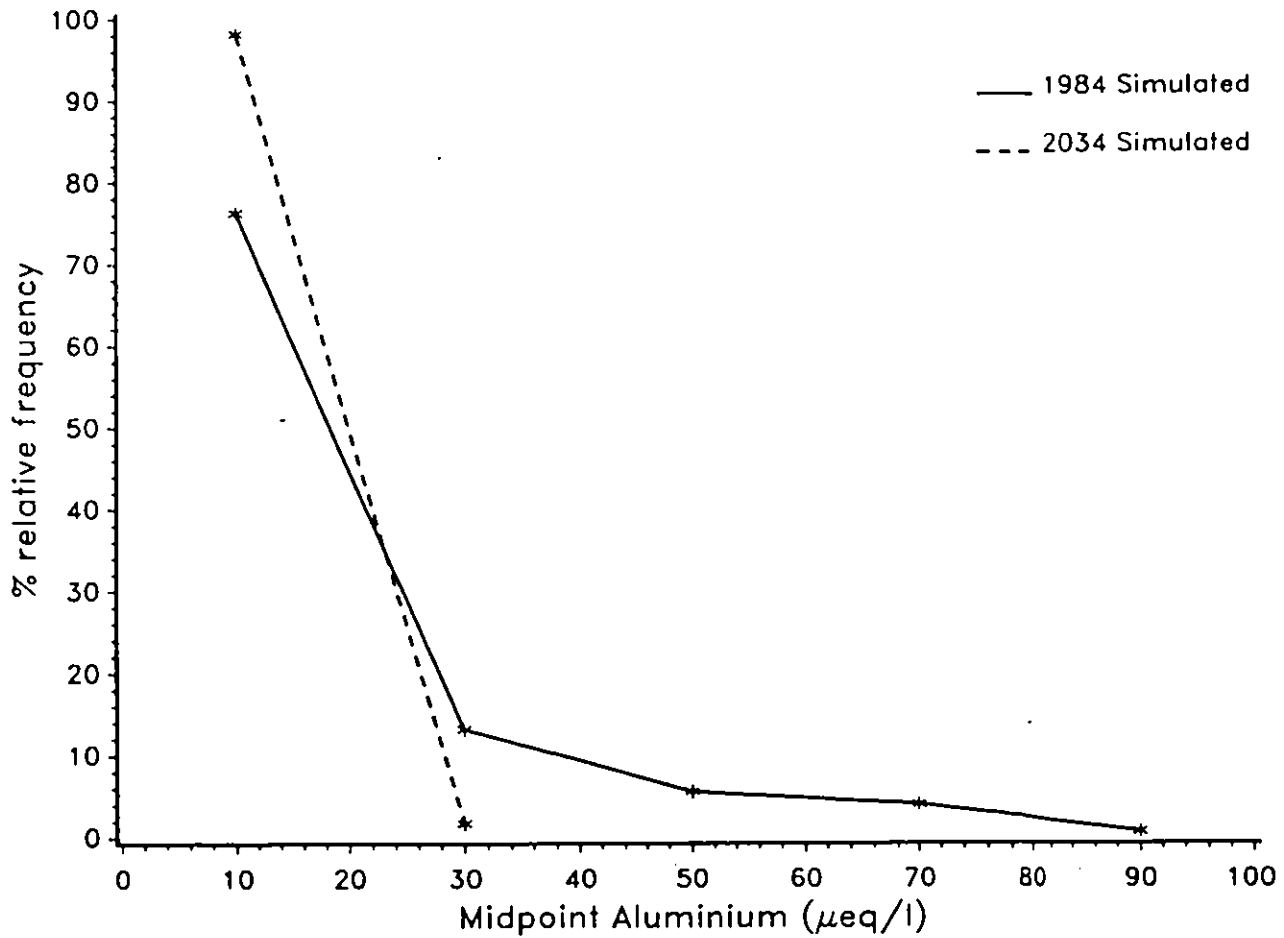
ALKALINITY

Figure D2 (a)



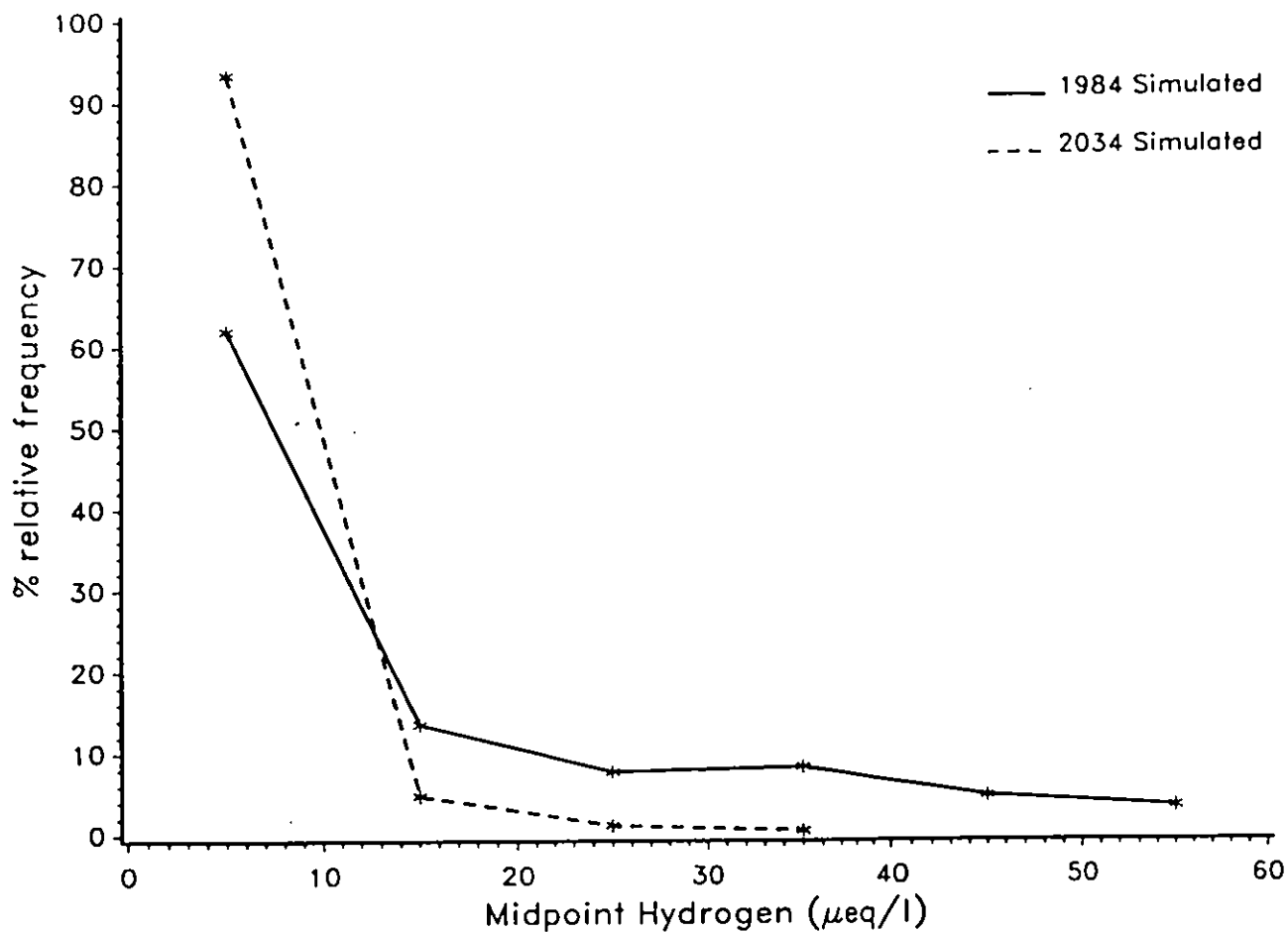
ALUMINIUM

Figure D2 (b)



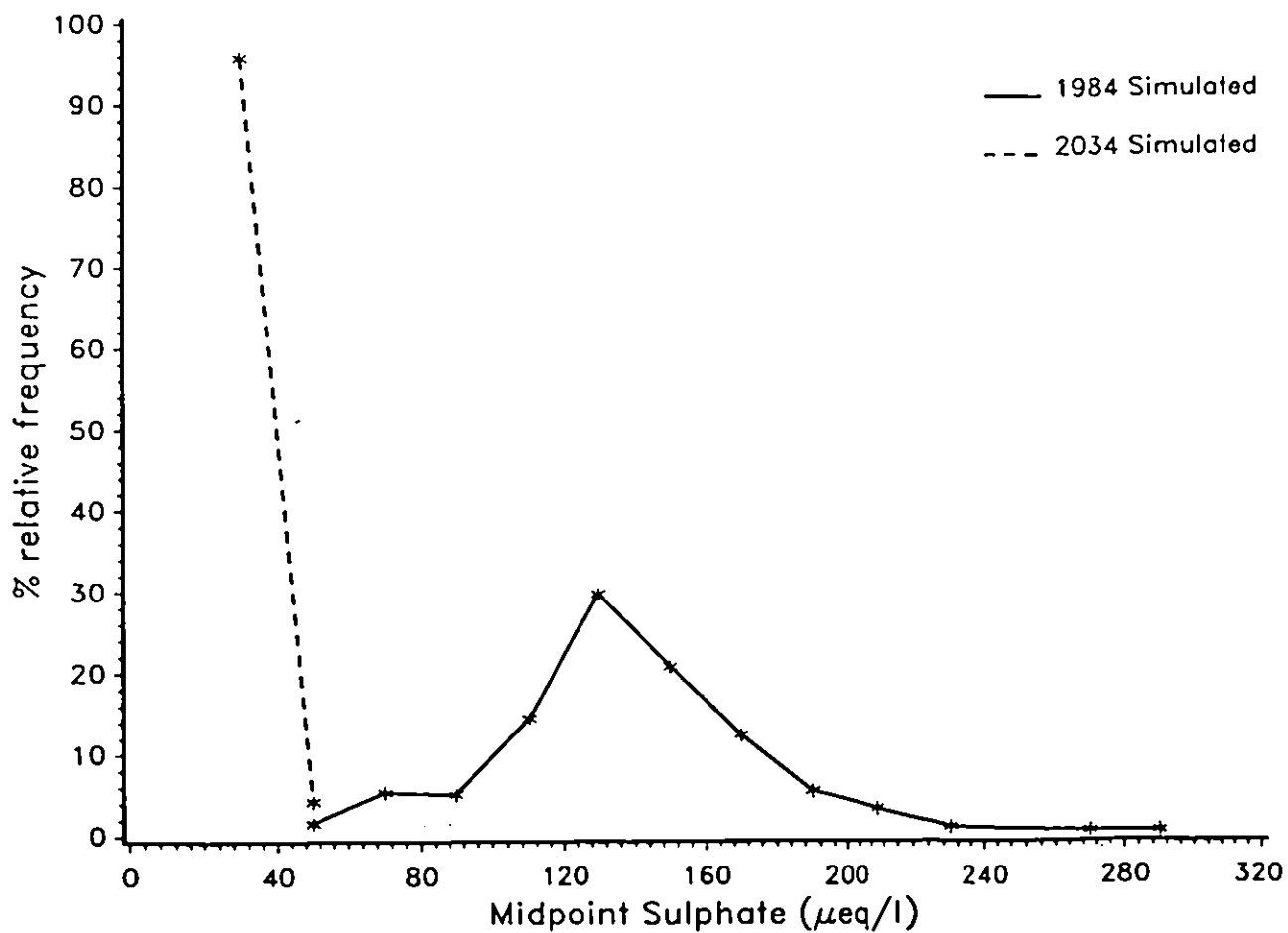
HYDROGEN

Figure D2 (c)



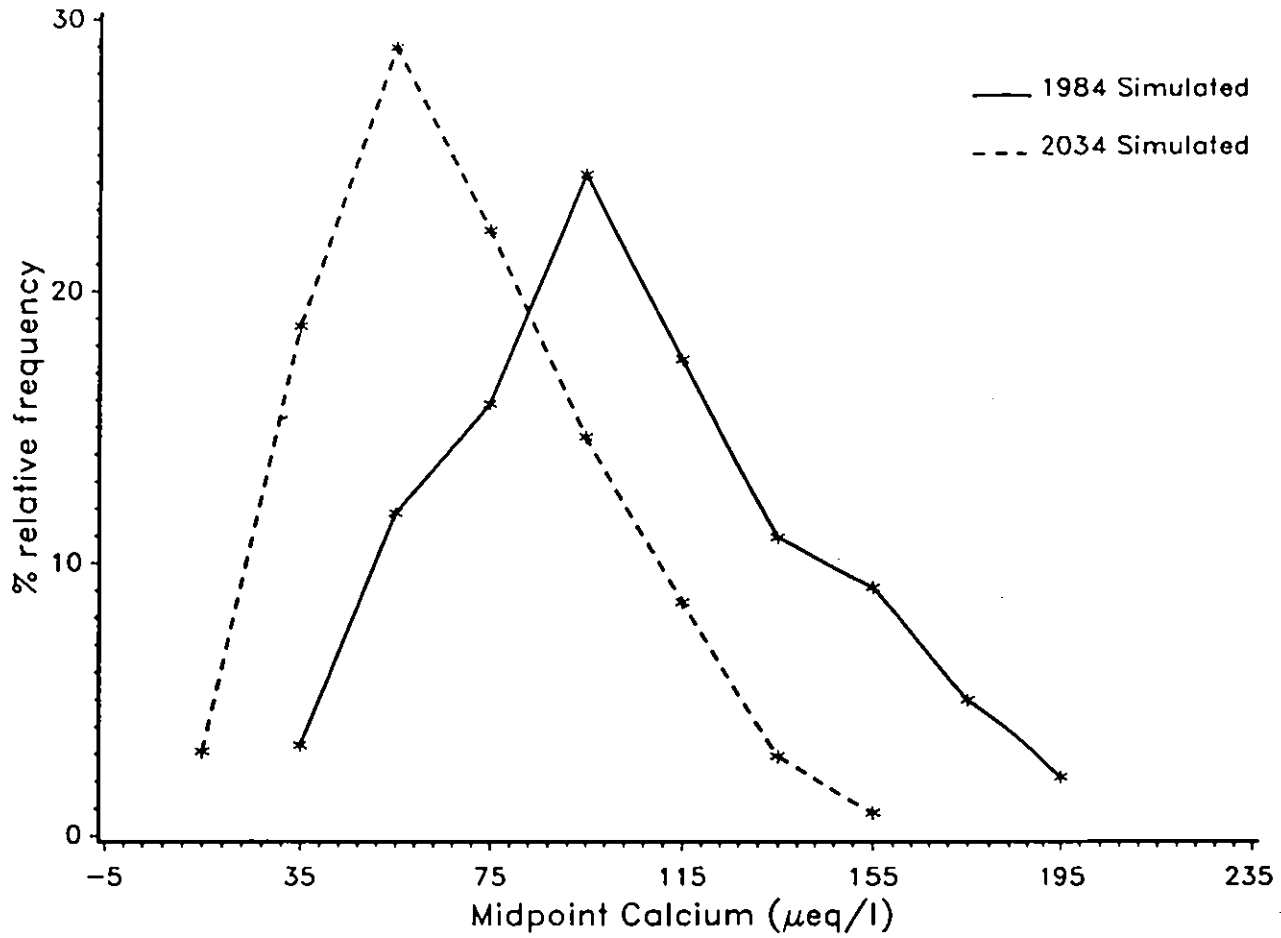
SULPHATE

Figure D2 (d)



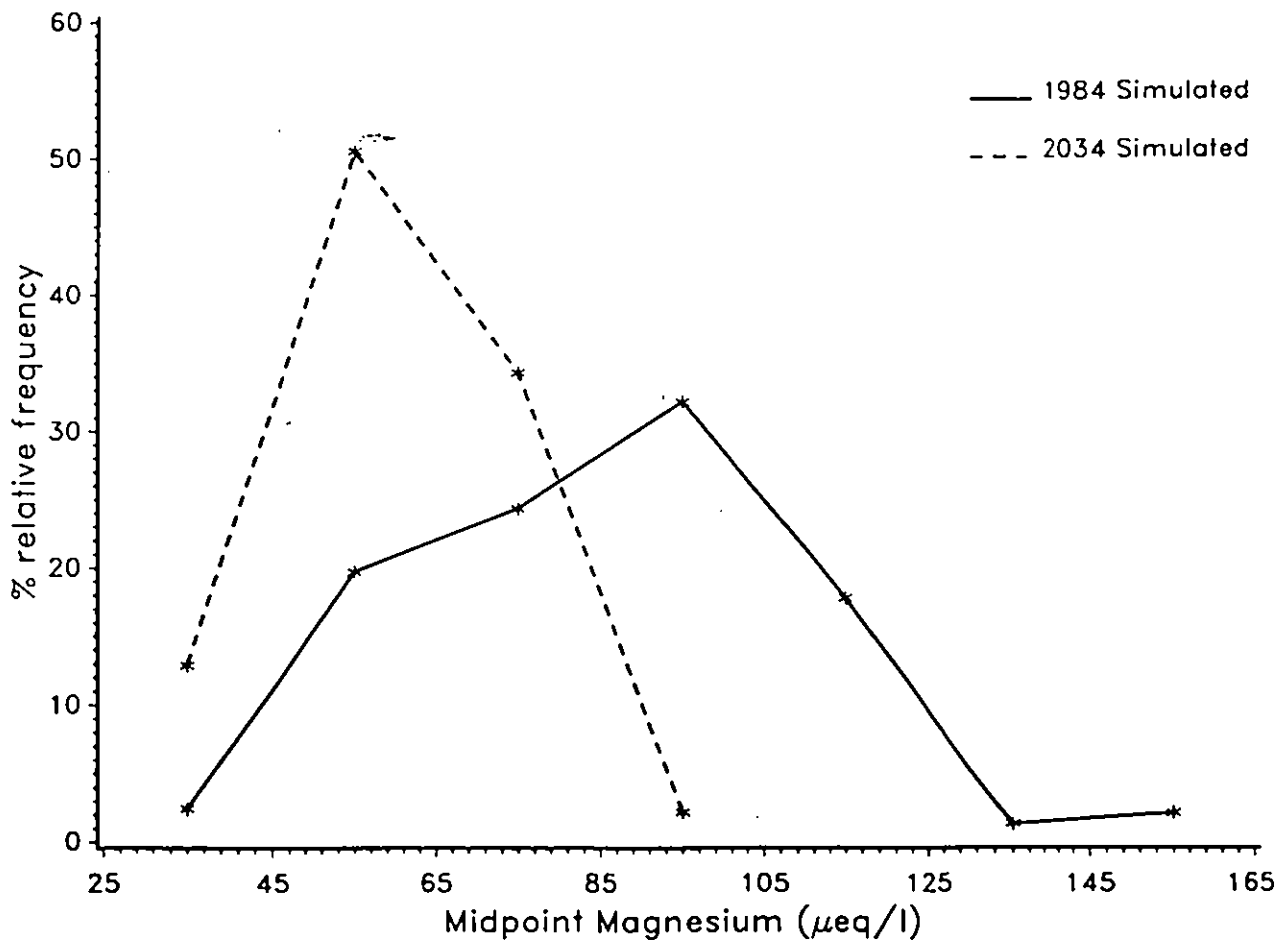
CALCIUM

Figure D2 (e)



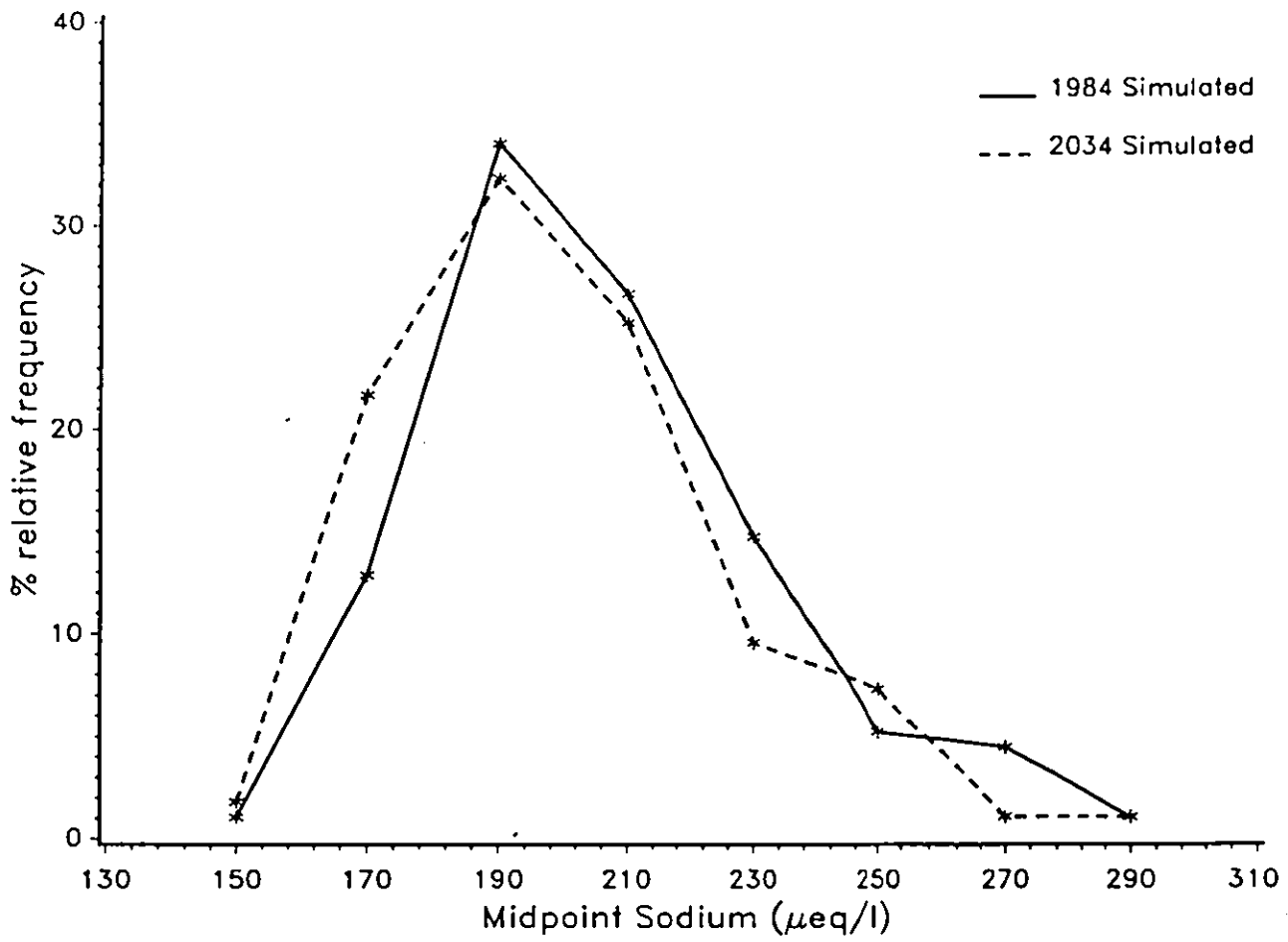
MAGNESIUM

Figure D2 (f)



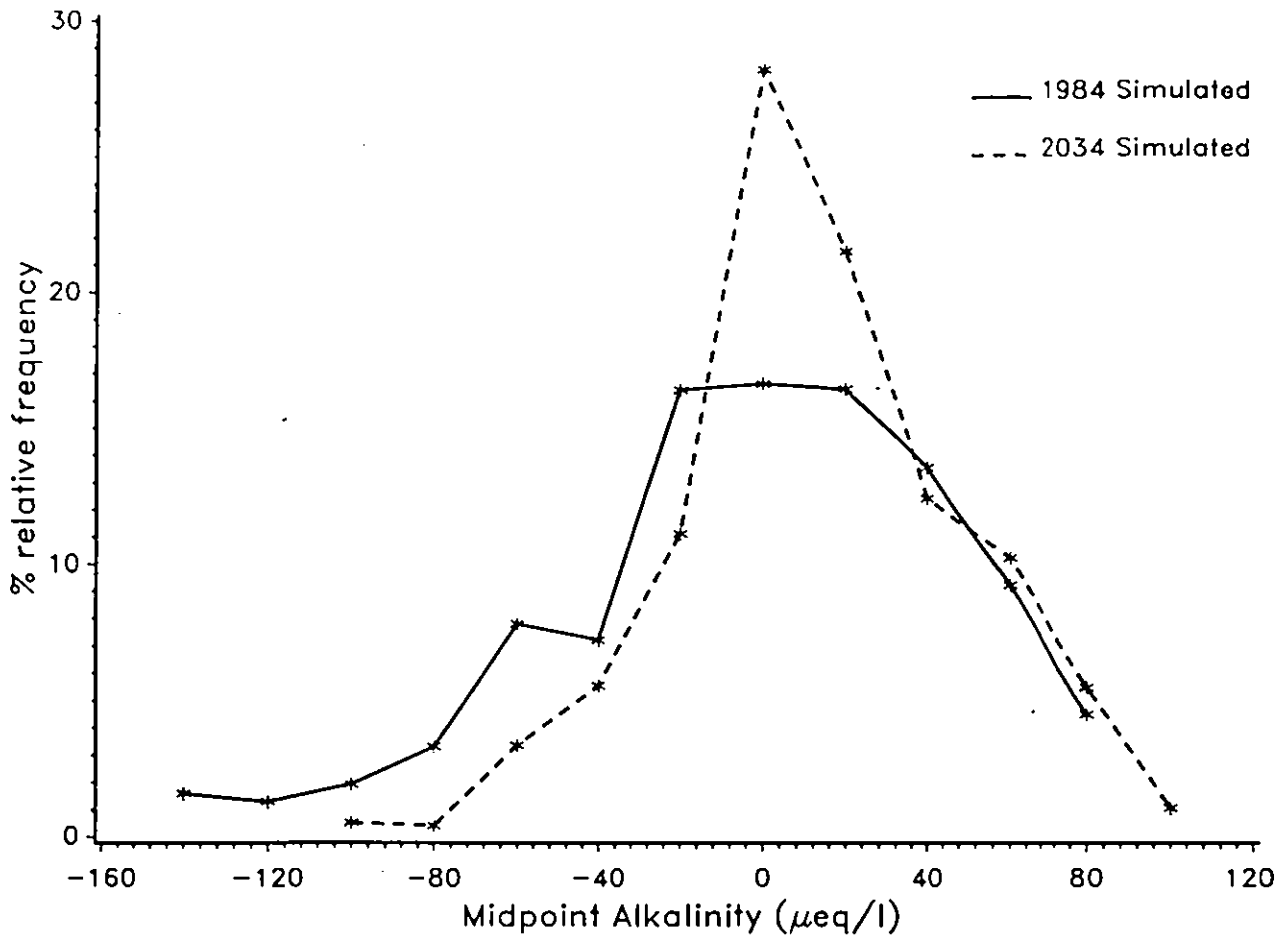
SODIUM

Figure D2 (g)



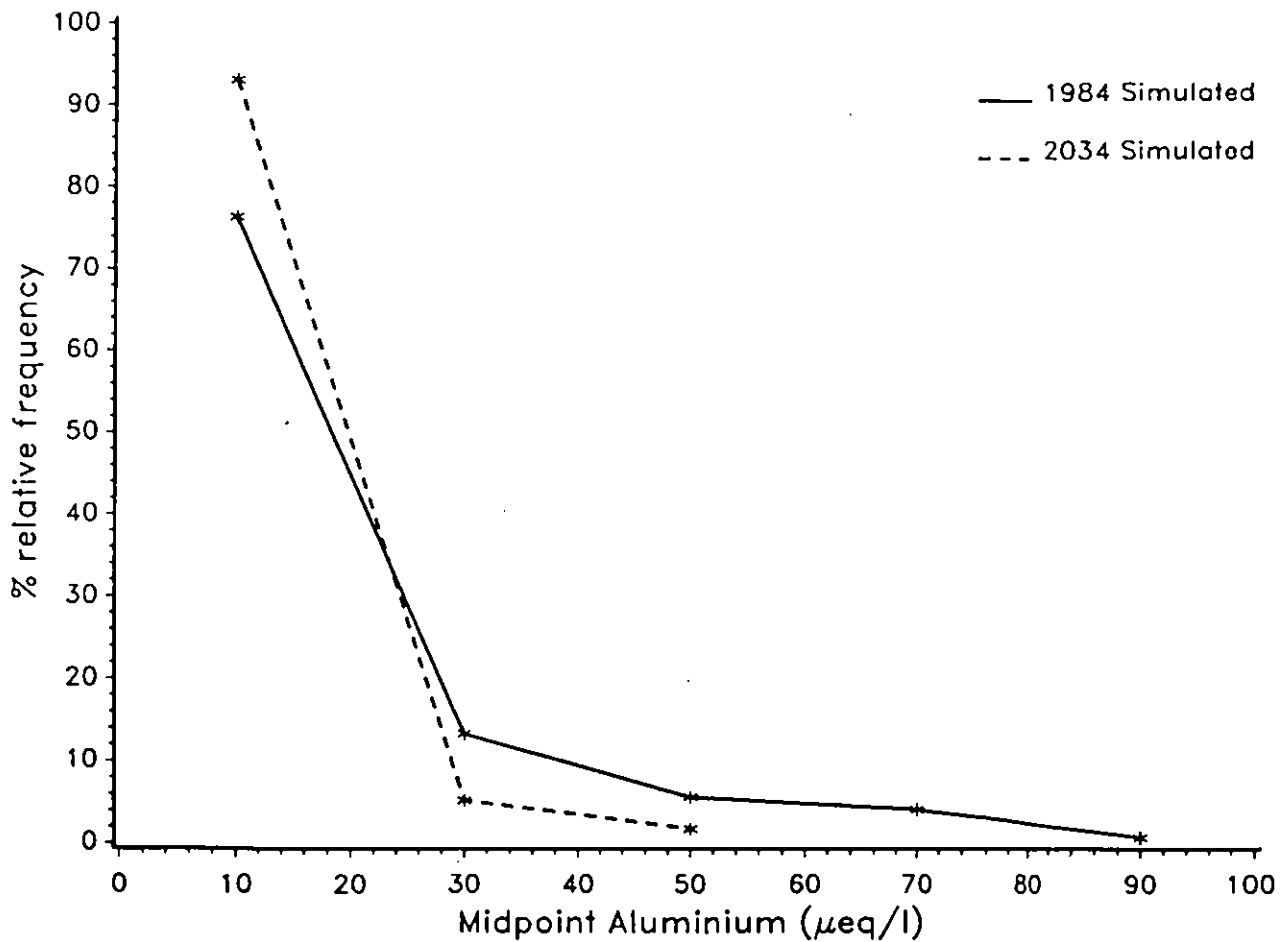
ALKALINITY

Figure D3 (a)



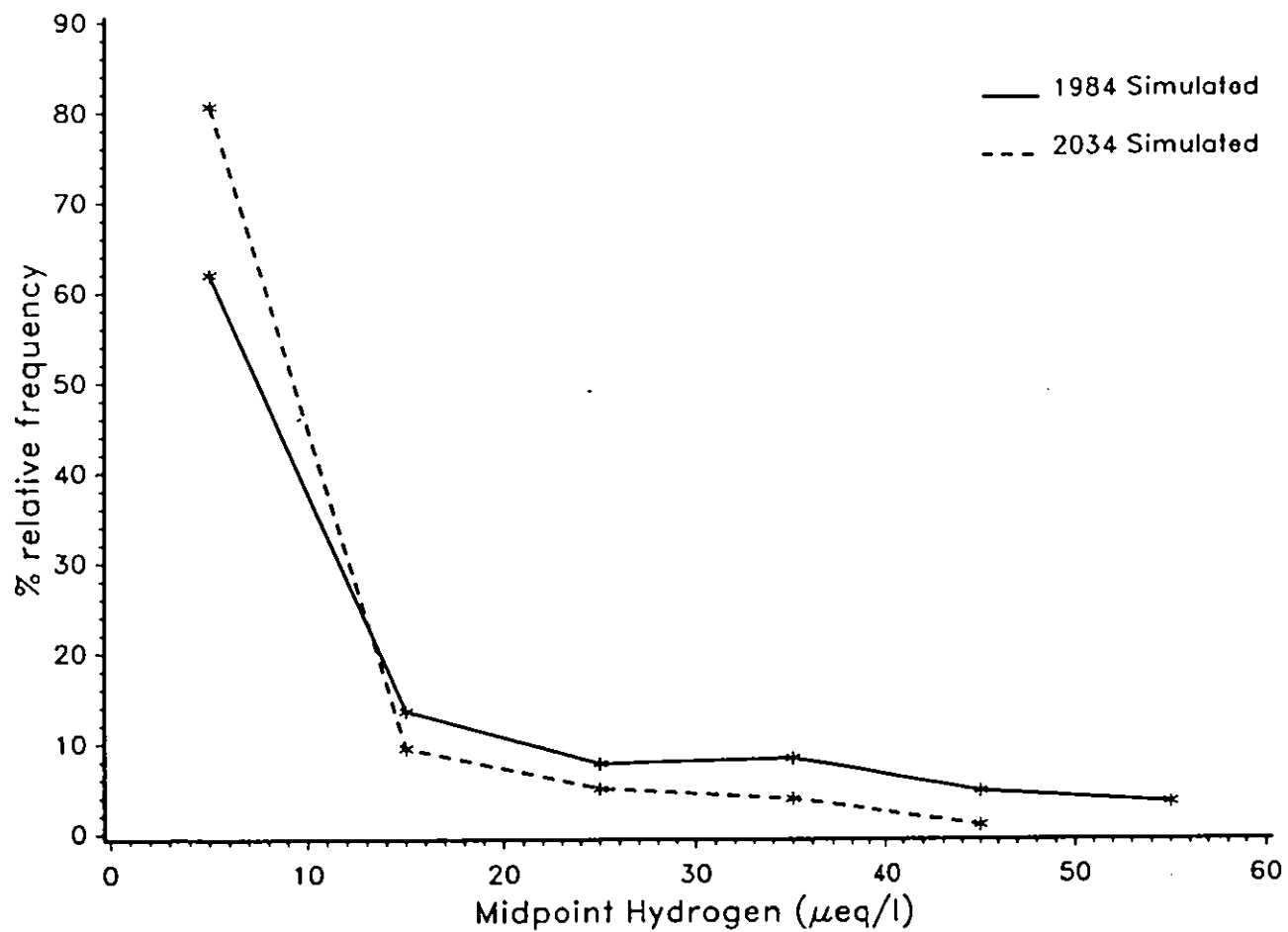
ALUMINIUM

Figure D3 (b)



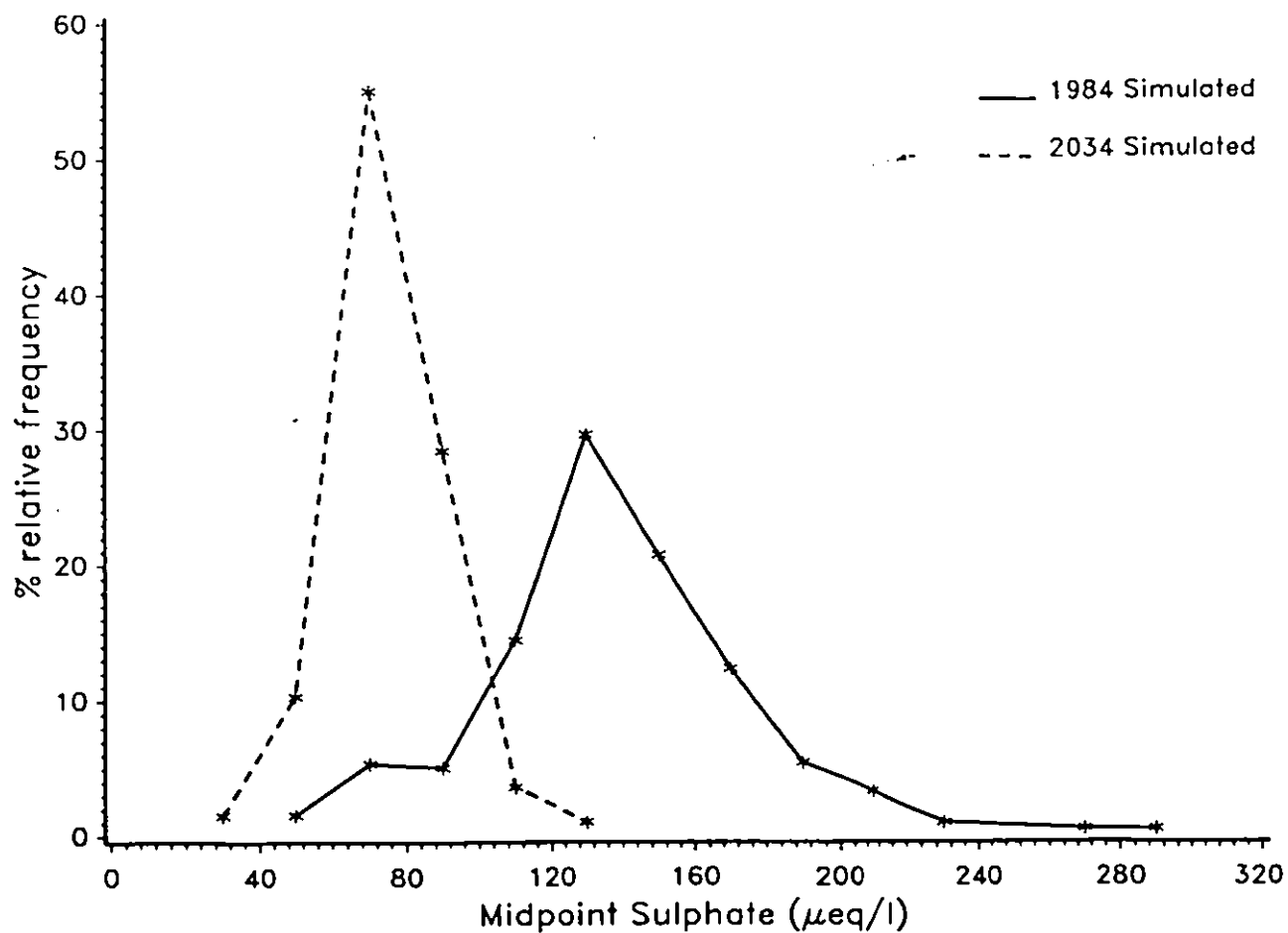
HYDROGEN

Figure D3 (c)



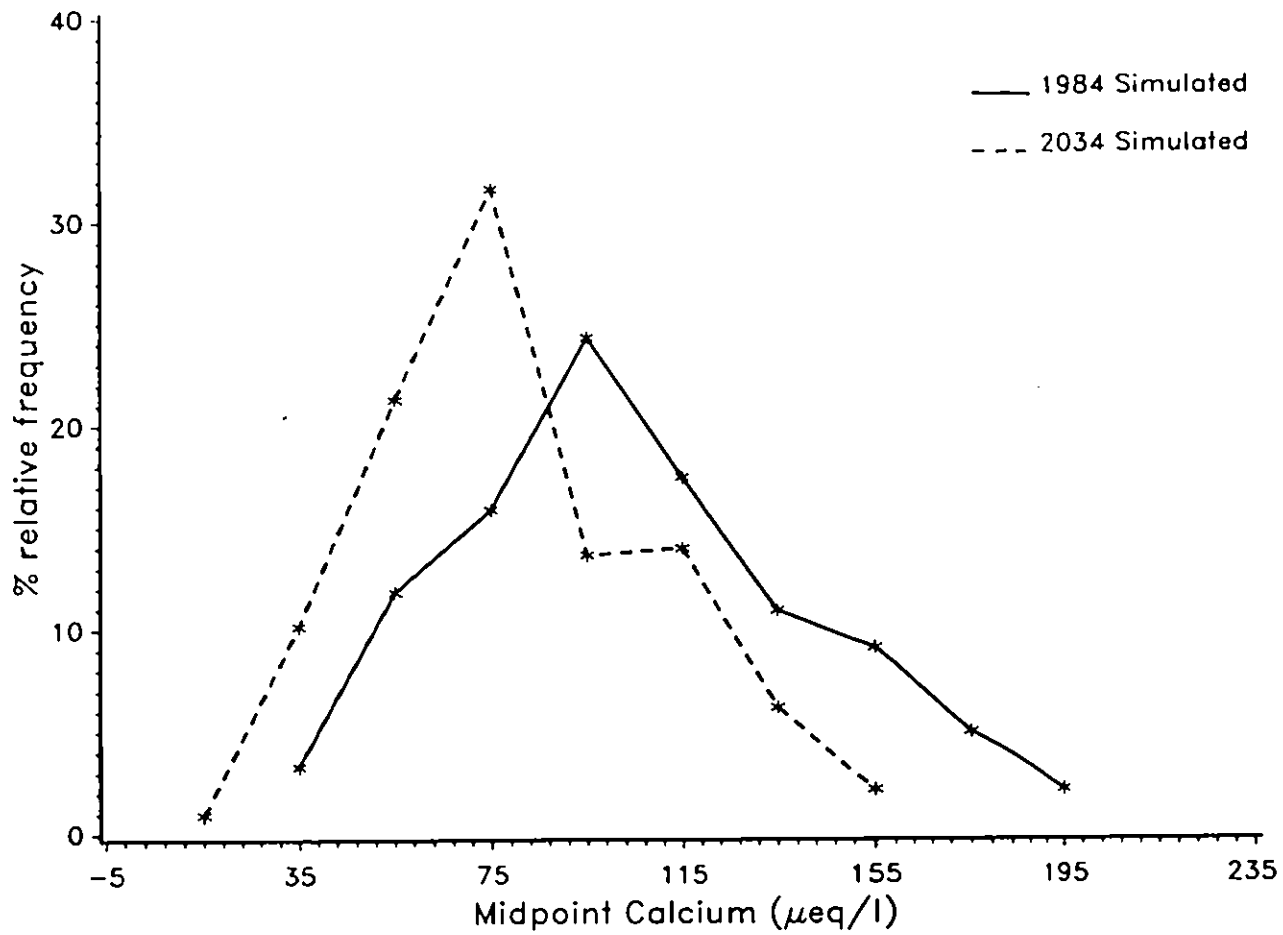
SULPHATE

Figure D3 (d)



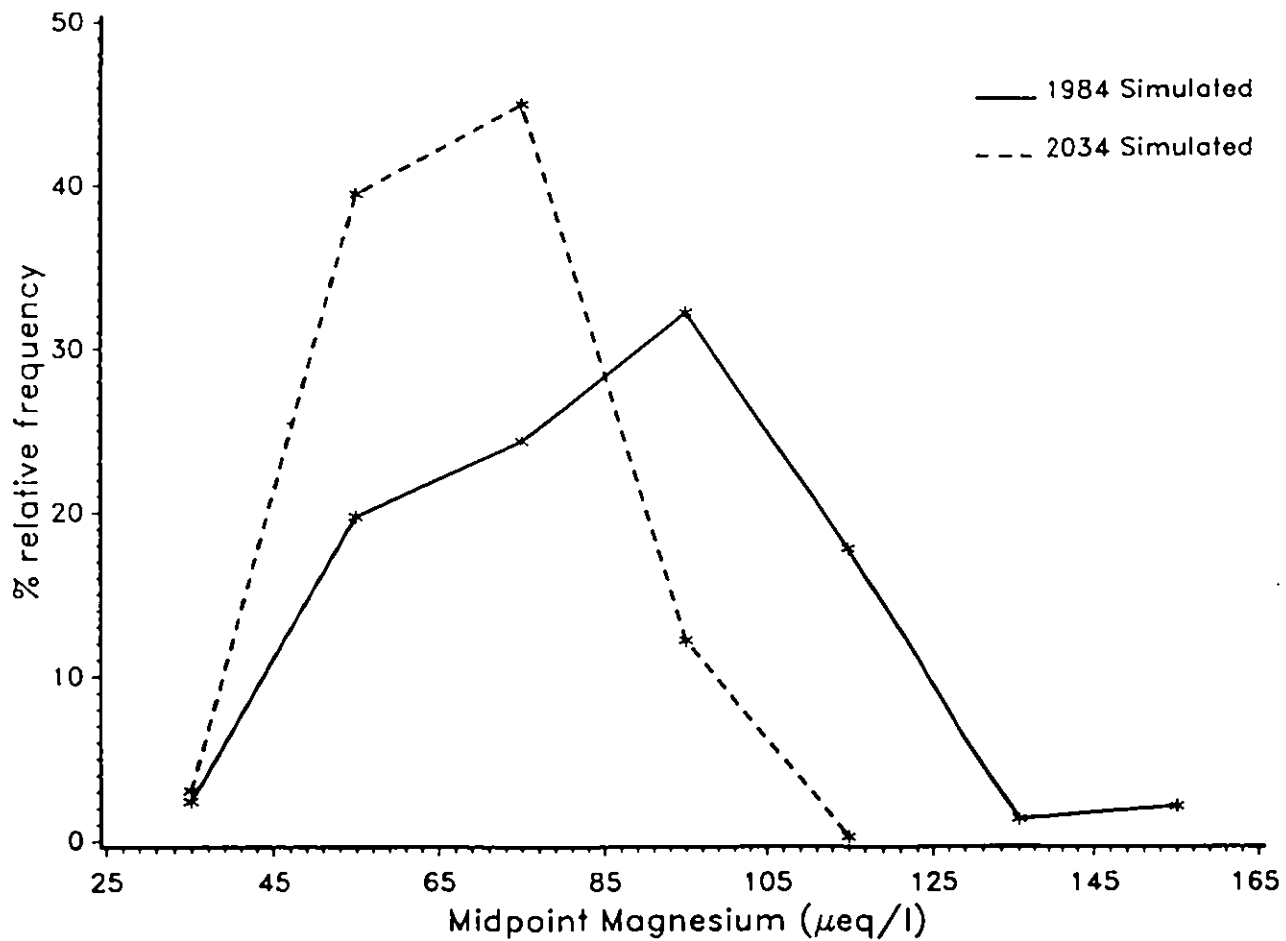
CALCIUM

Figure D3 (e)



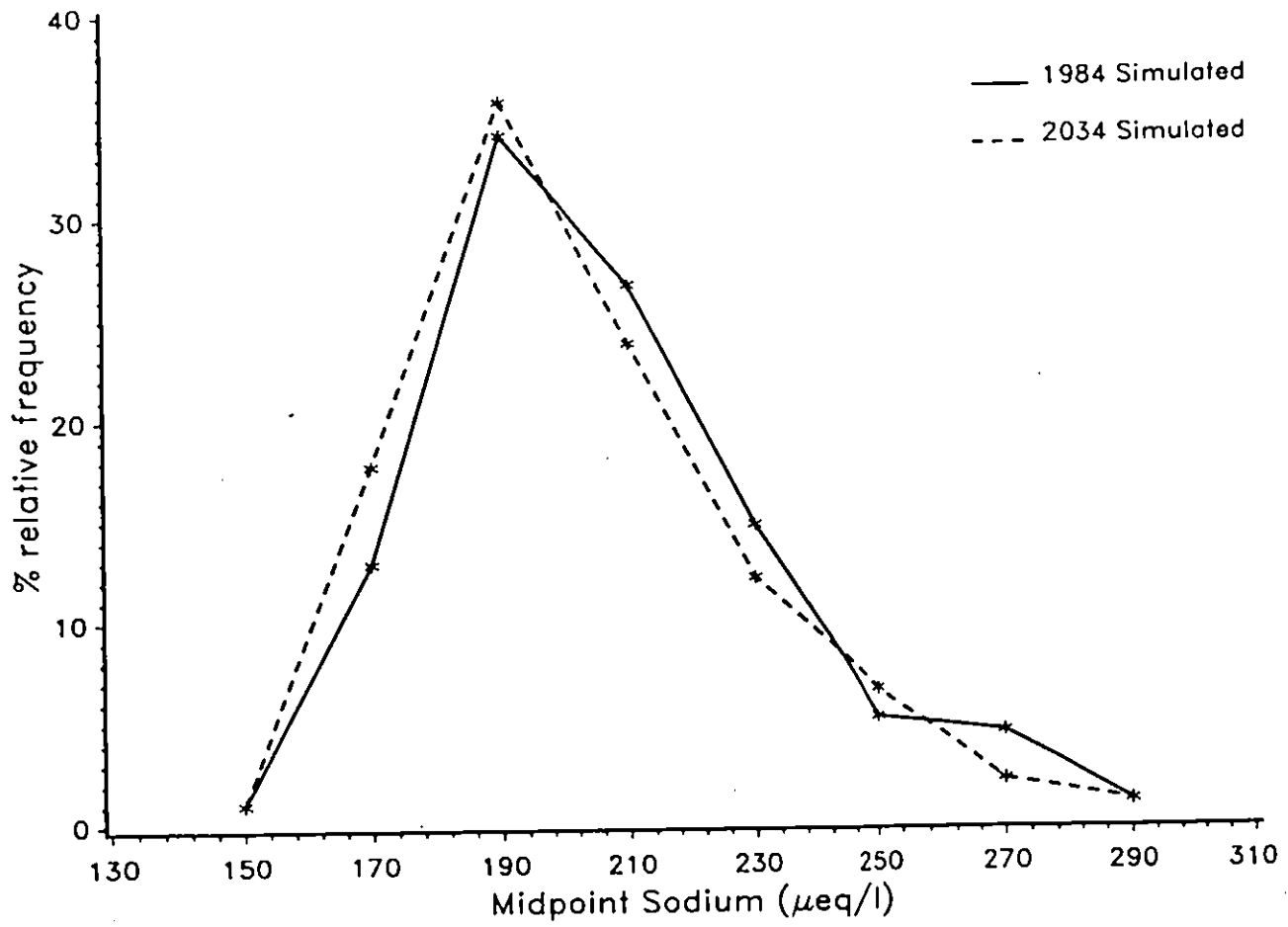
MAGNESIUM

Figure D3 (f)



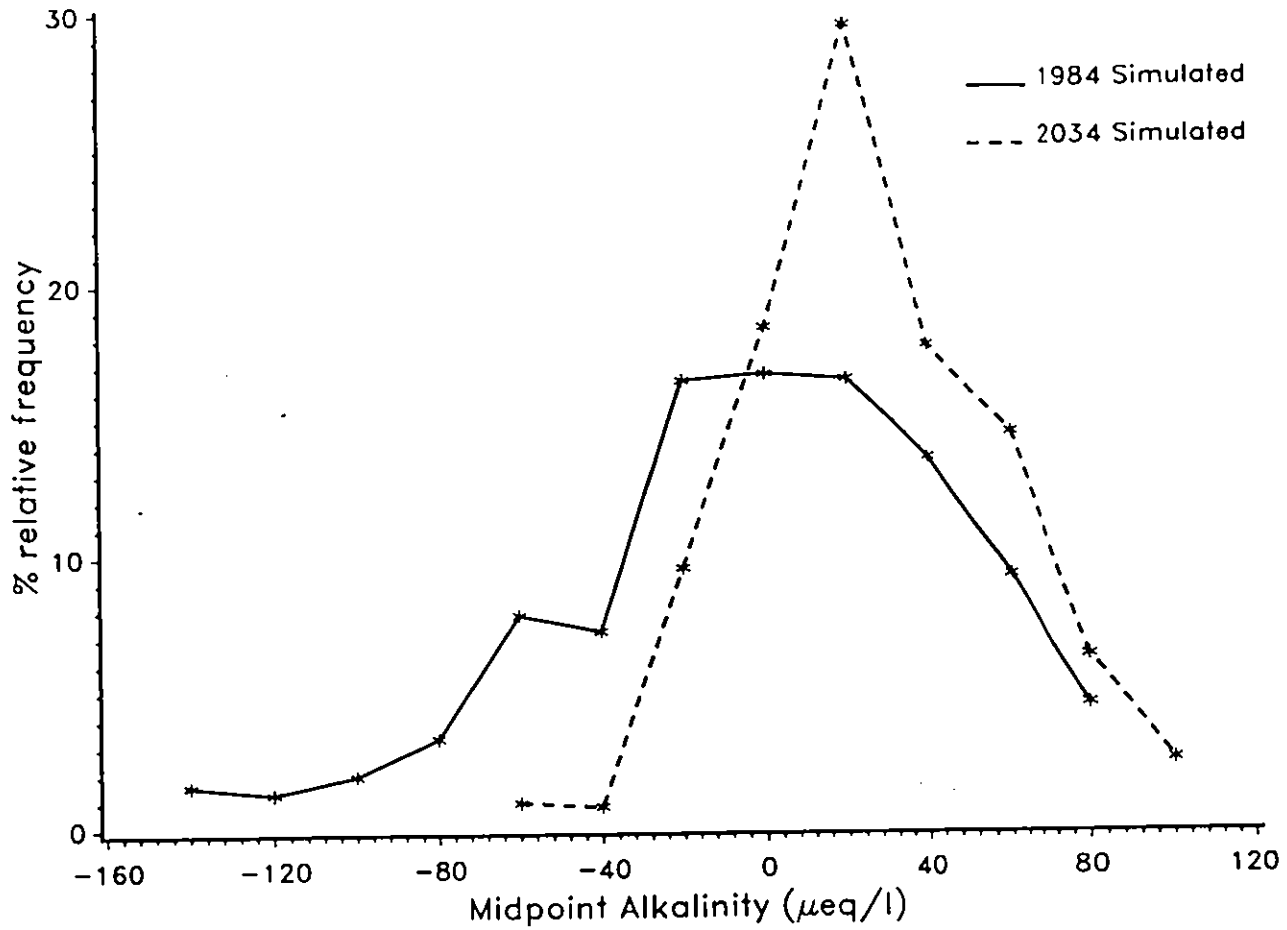
SODIUM

Figure D3 (g)



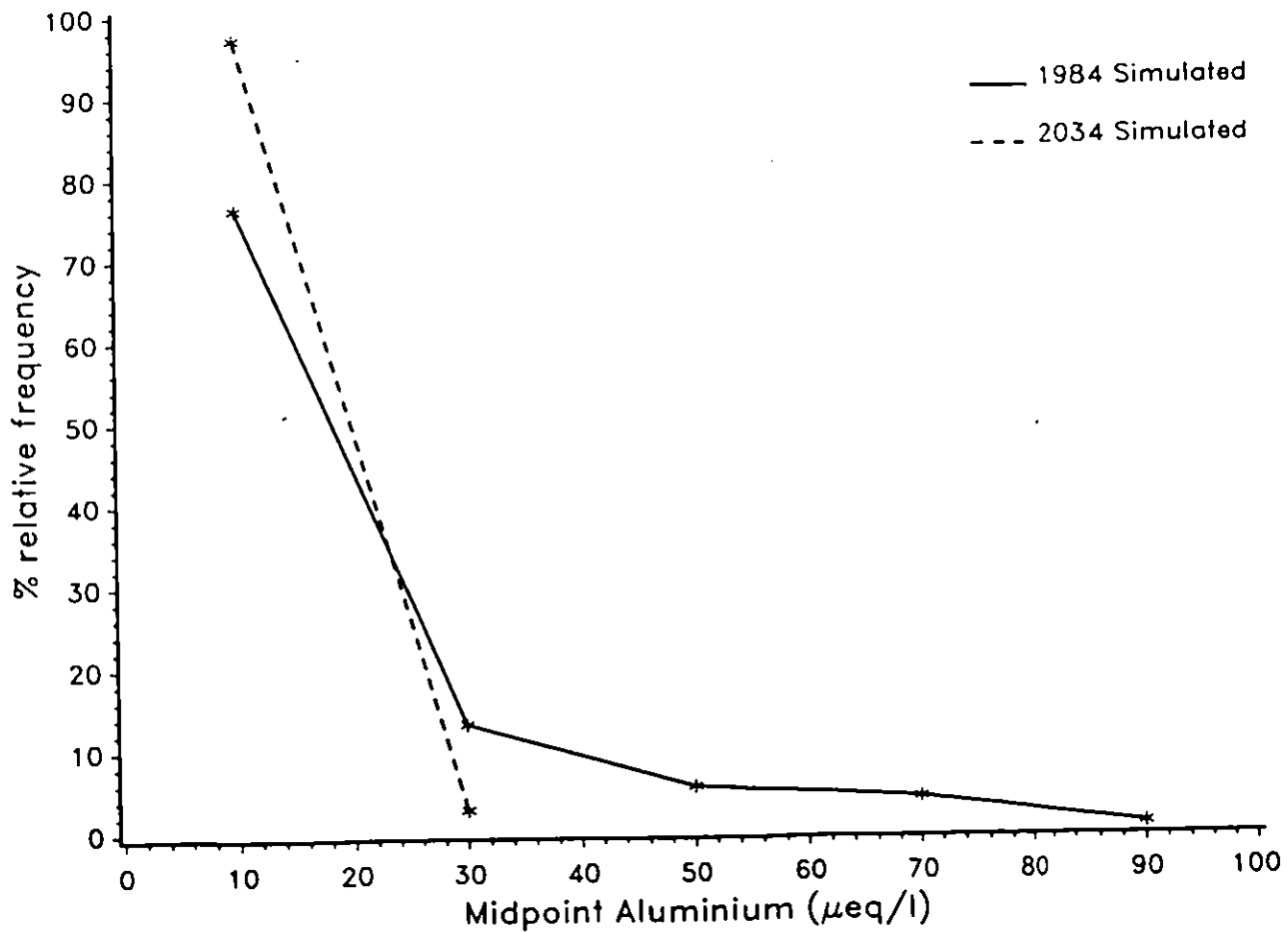
ALKALINITY

Figure D4 (a)



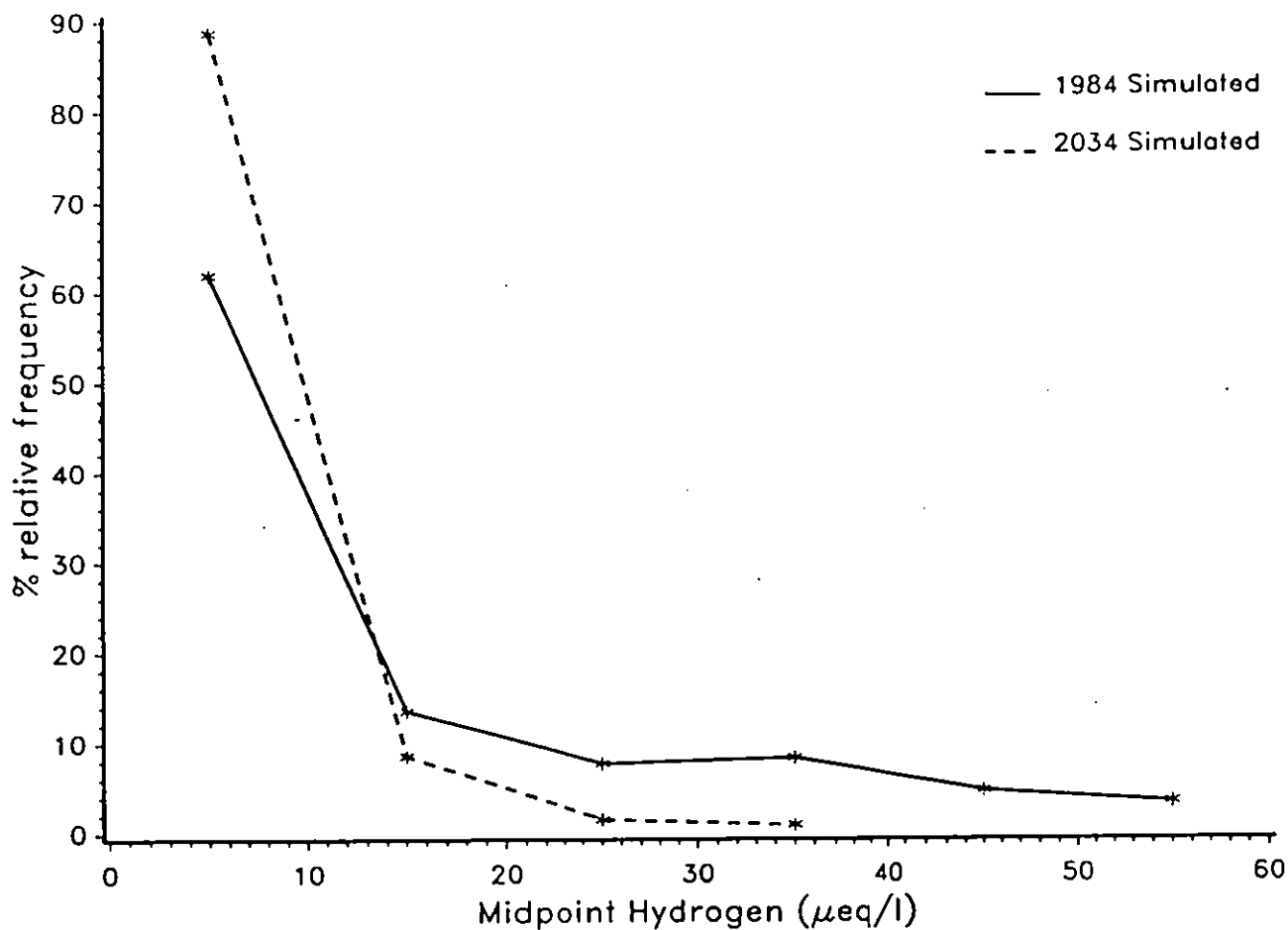
ALUMINIUM

Figure D4 (b)



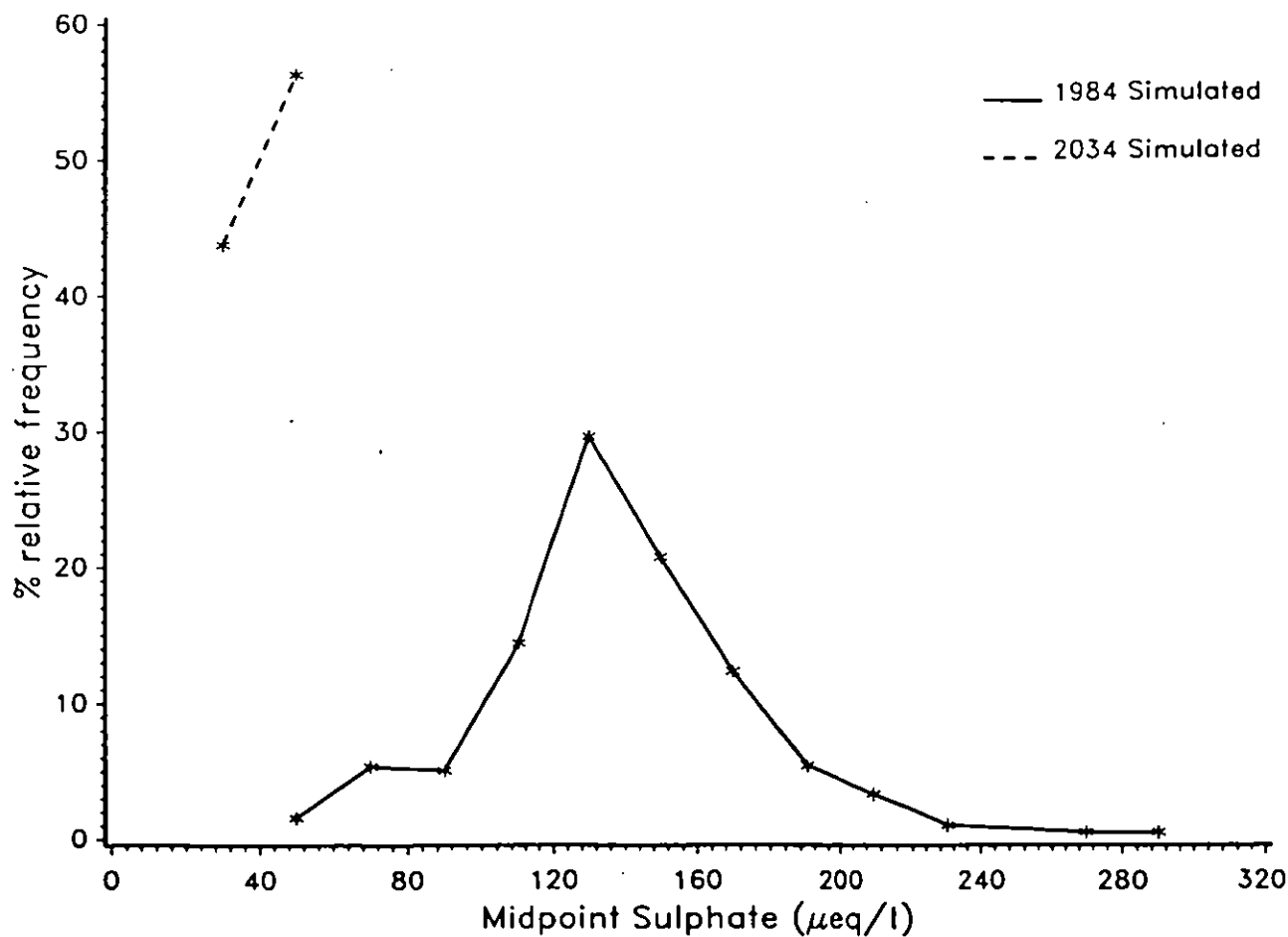
HYDROGEN

Figure D4 (c)



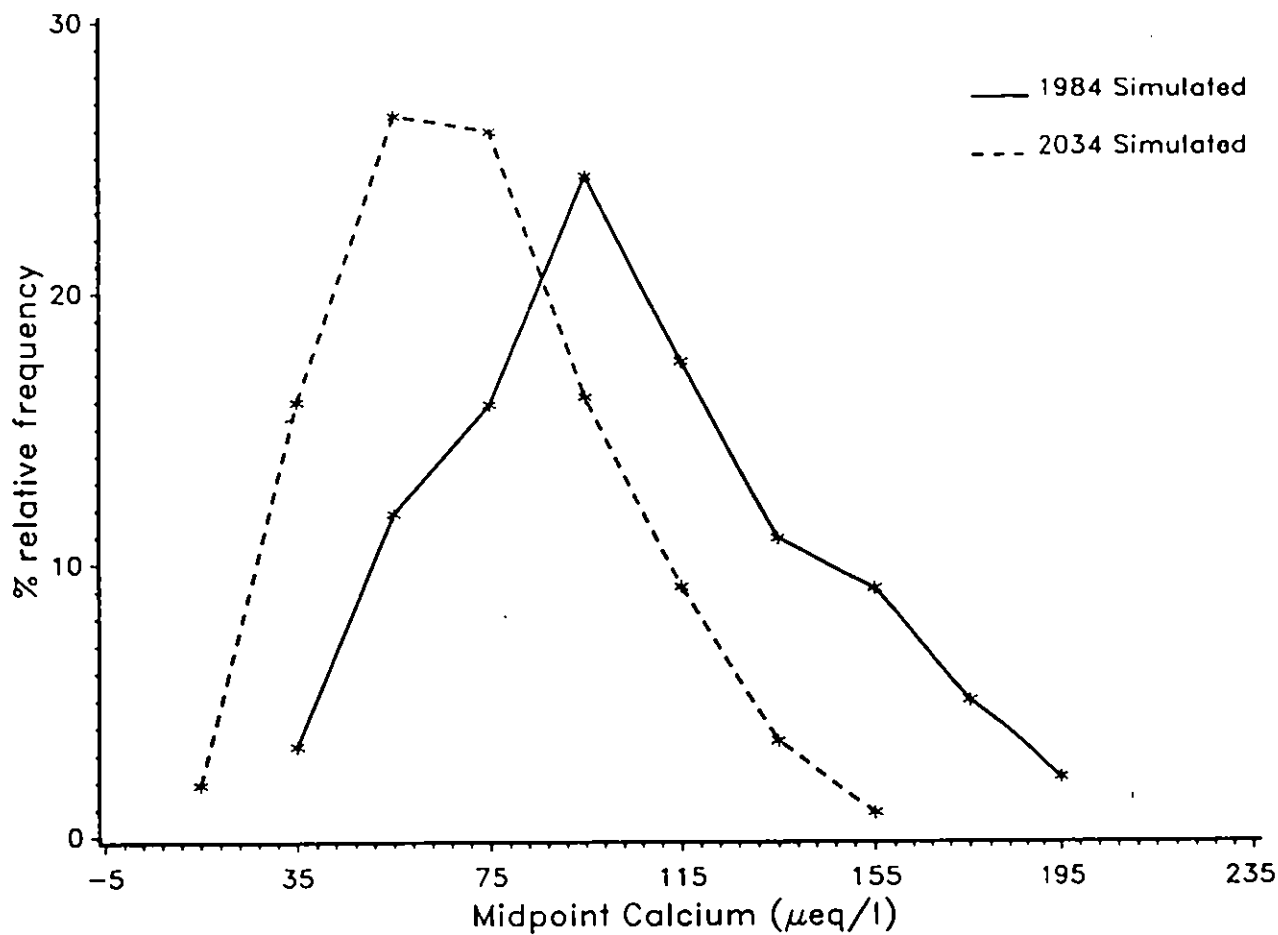
SULPHATE

Figure D4 (d)



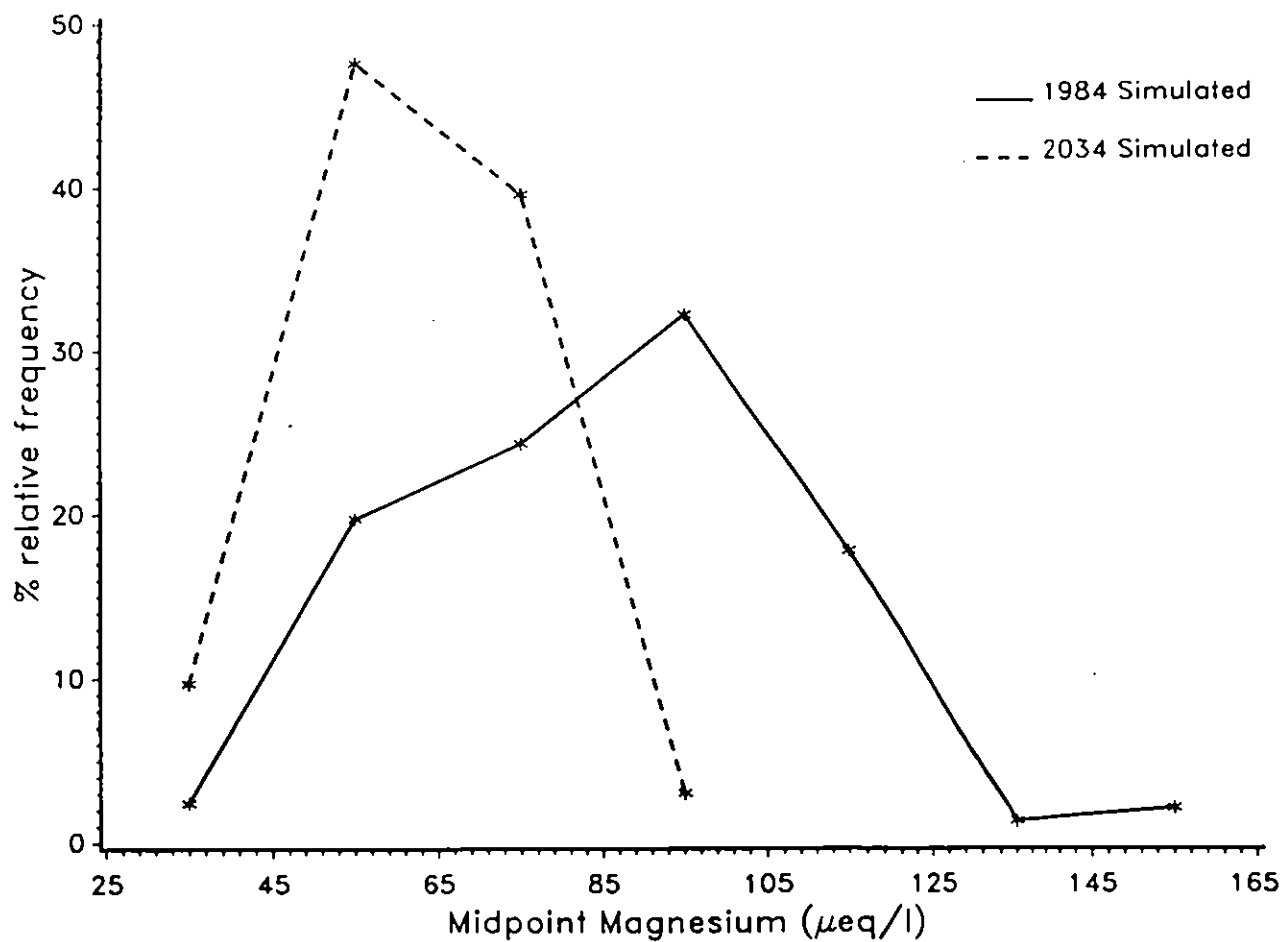
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Figure D4 (e)



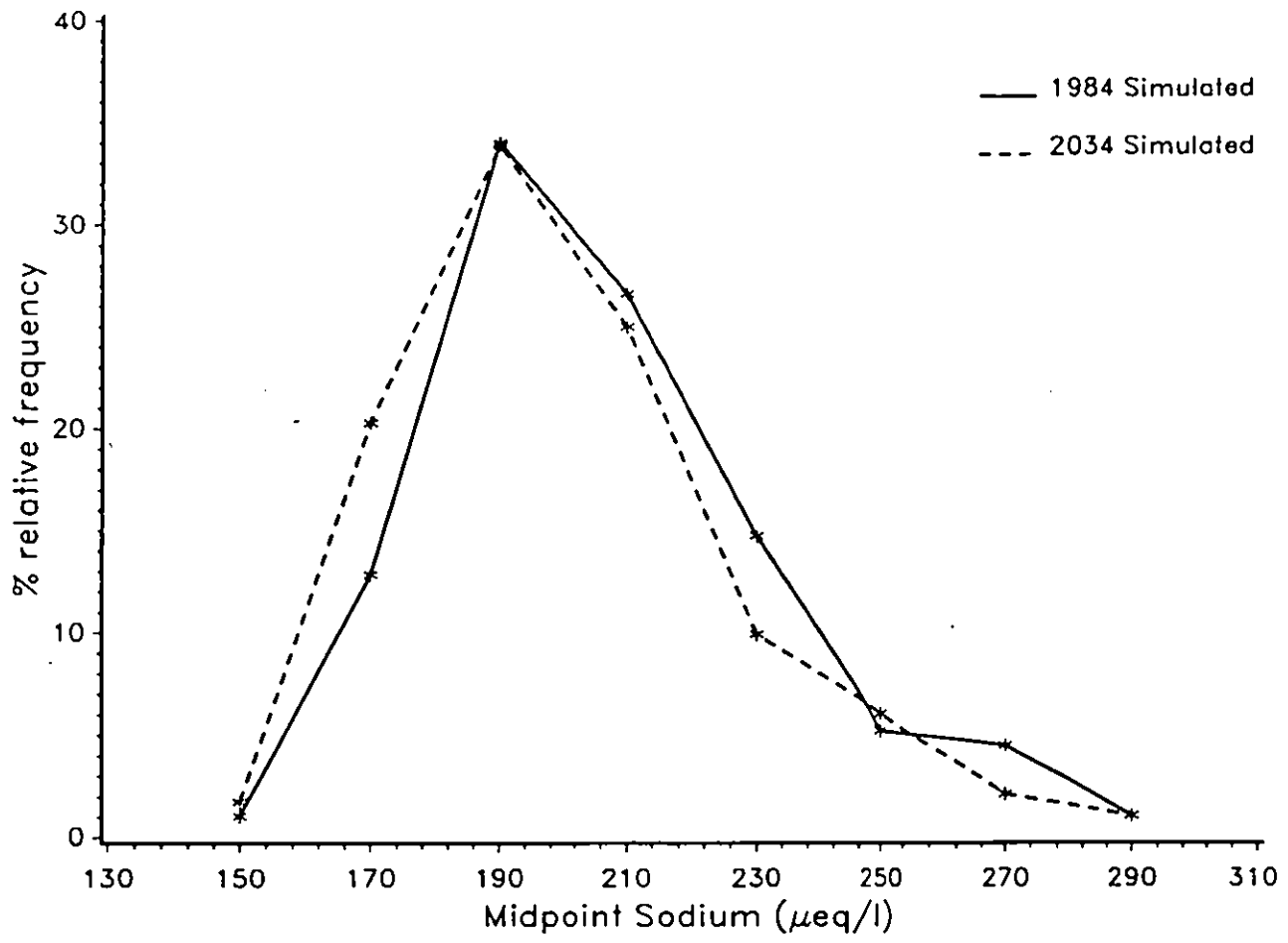
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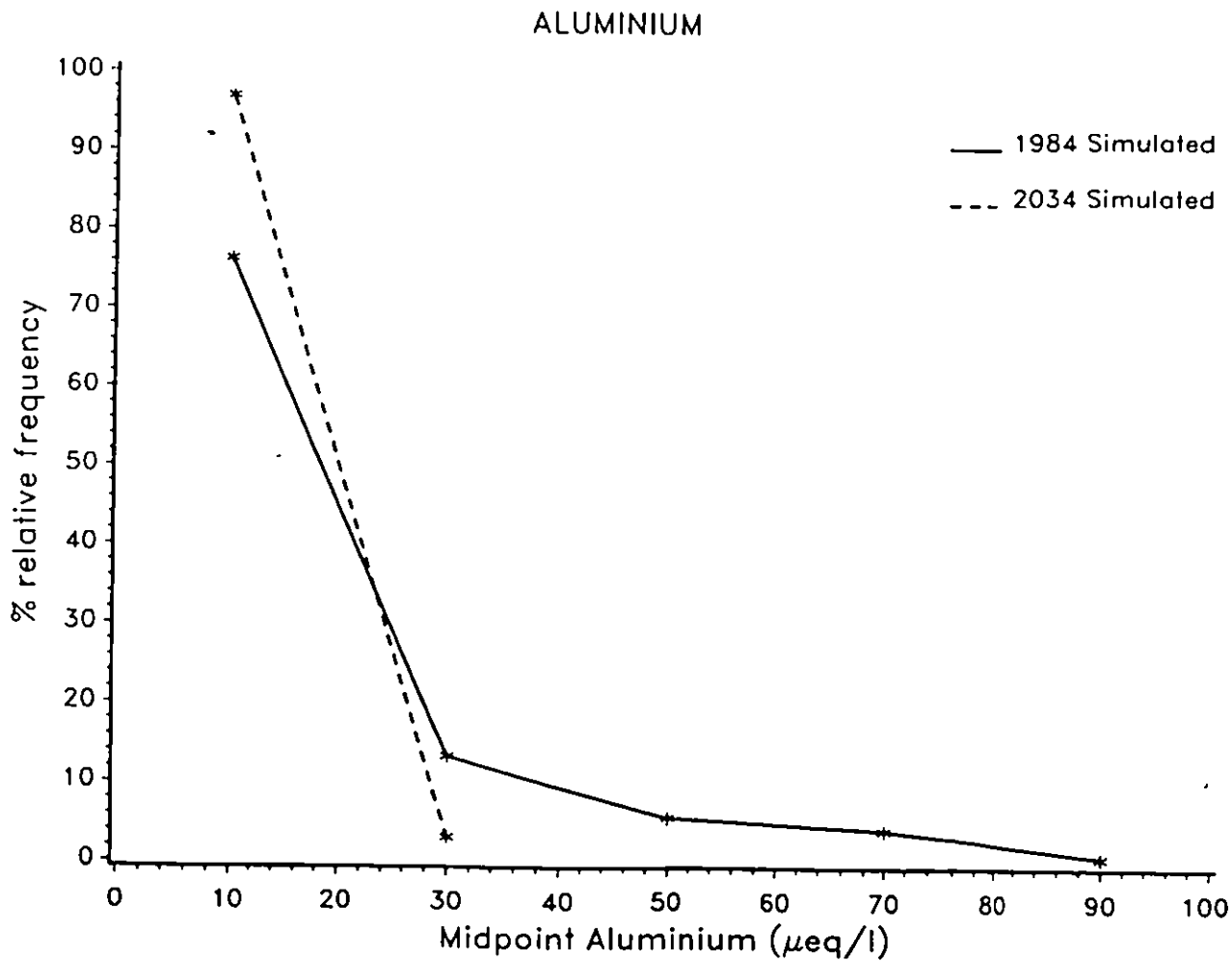
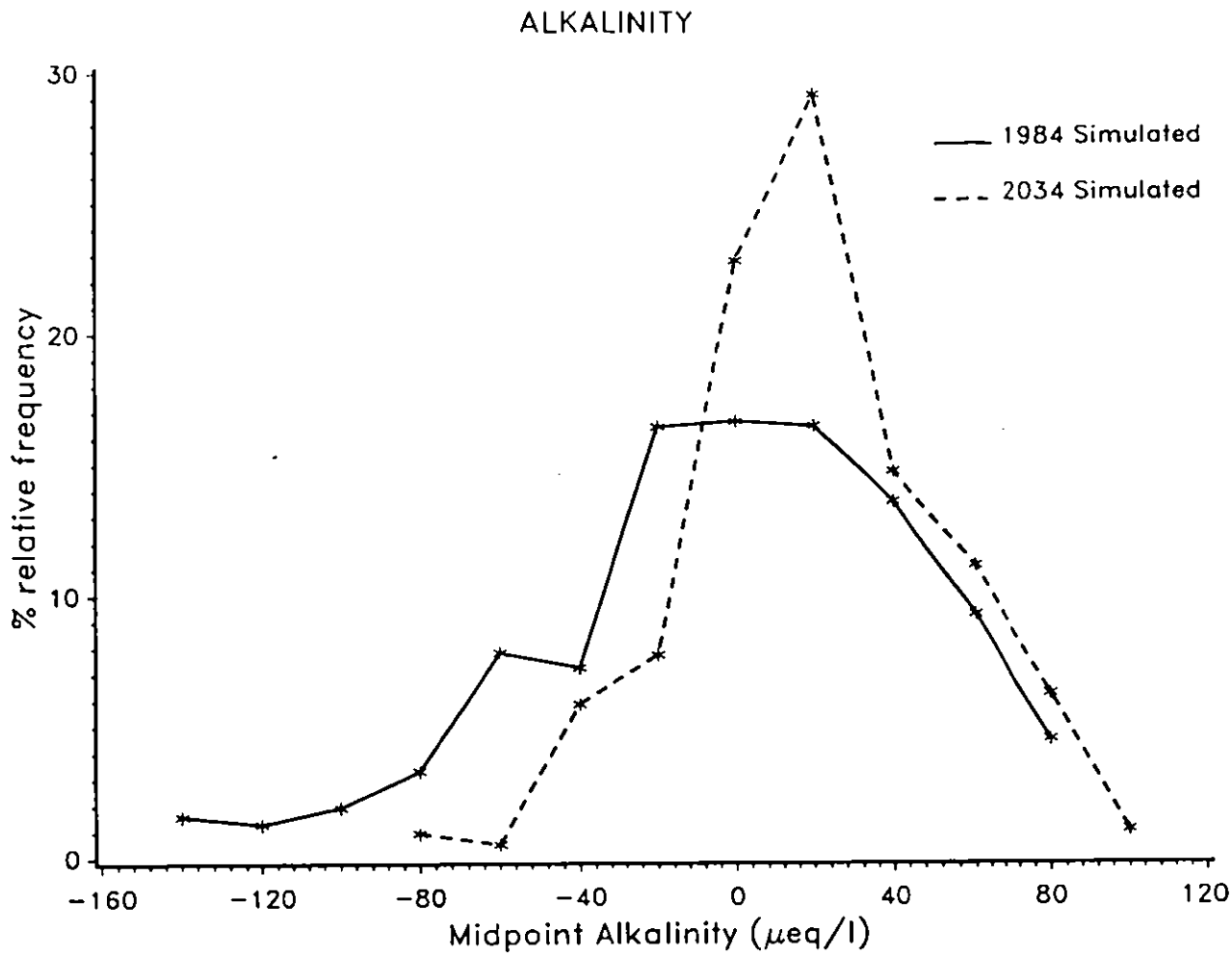
Figure D4 (f)



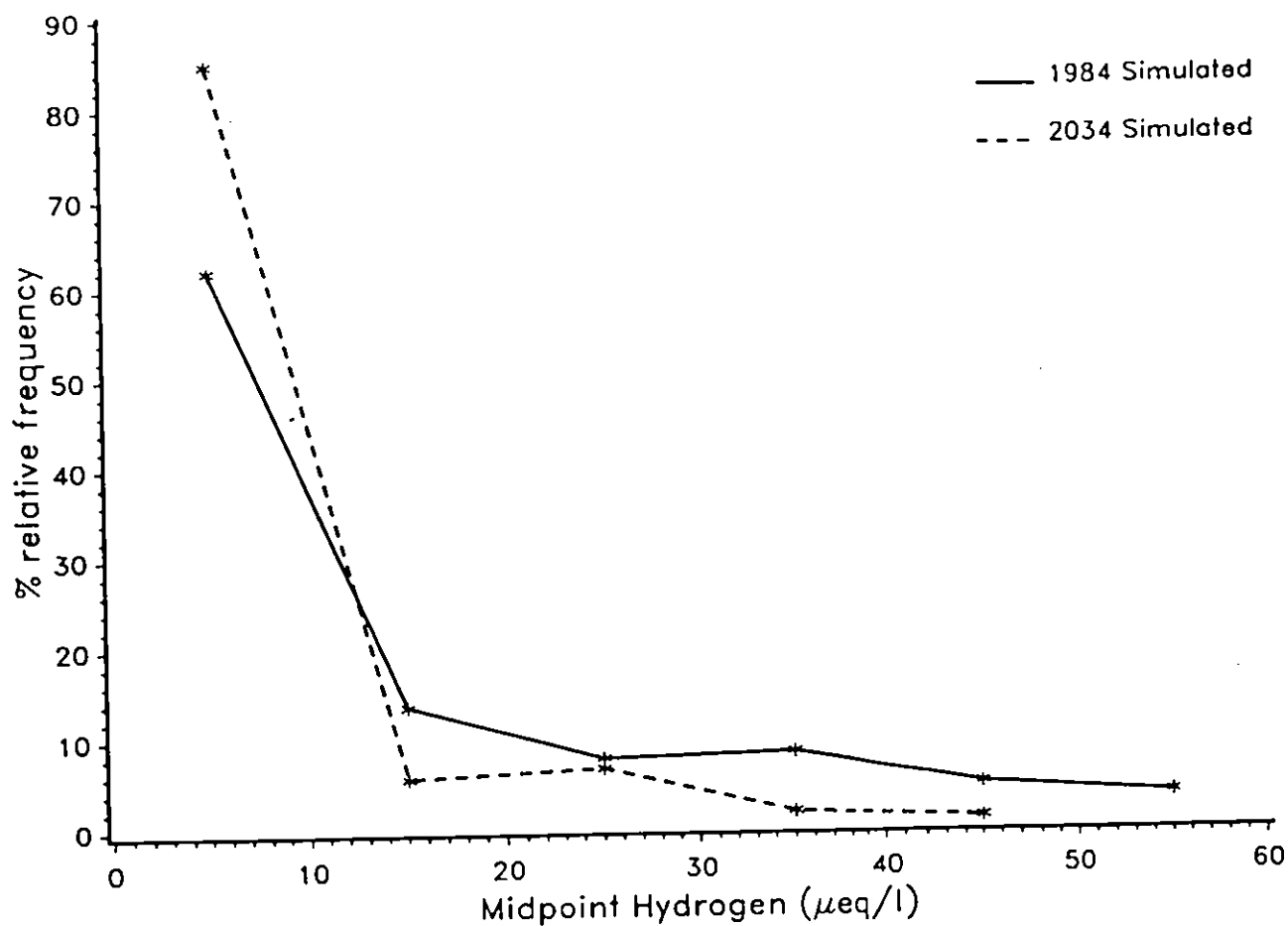
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Figure D4 (g)

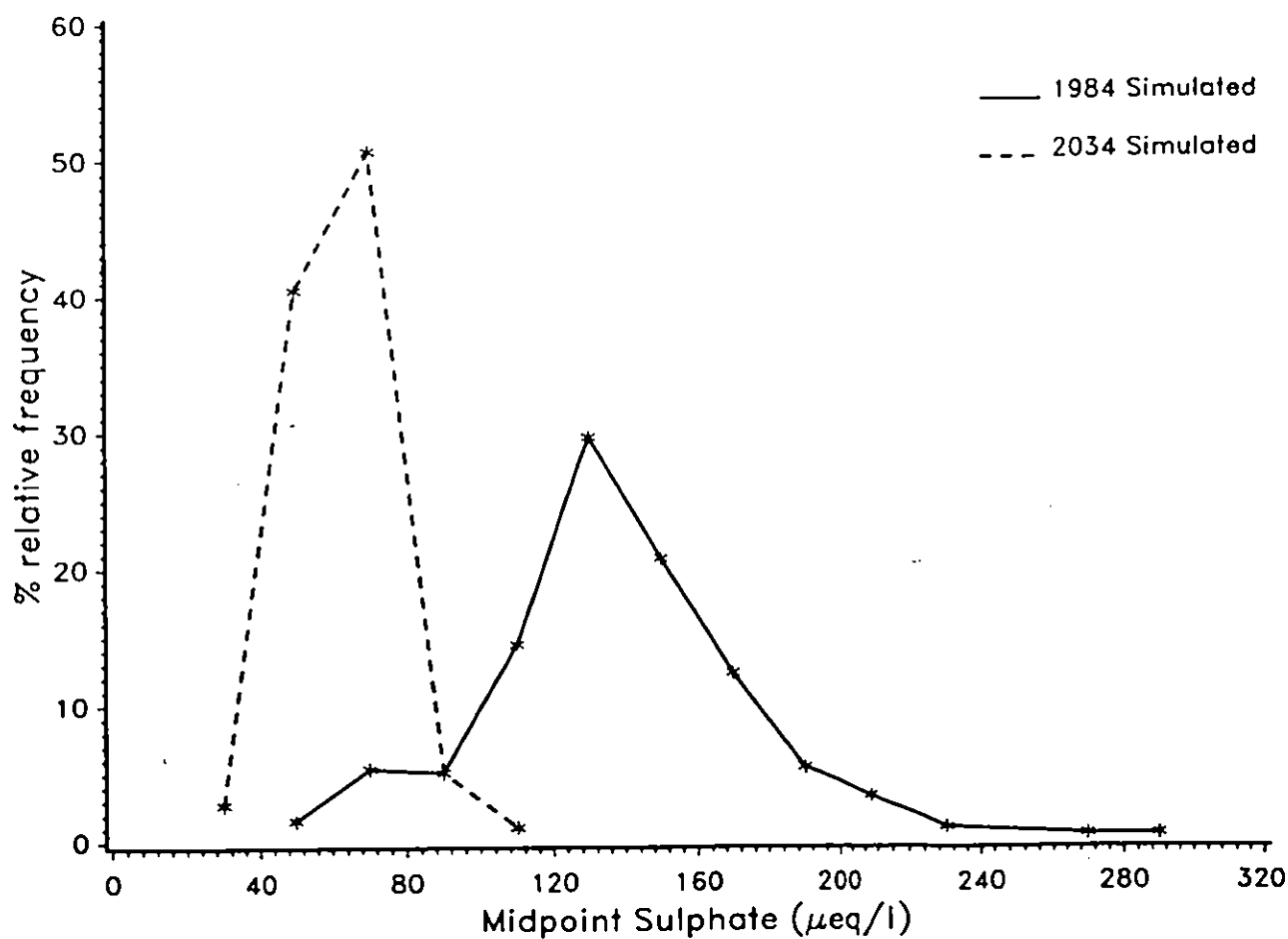




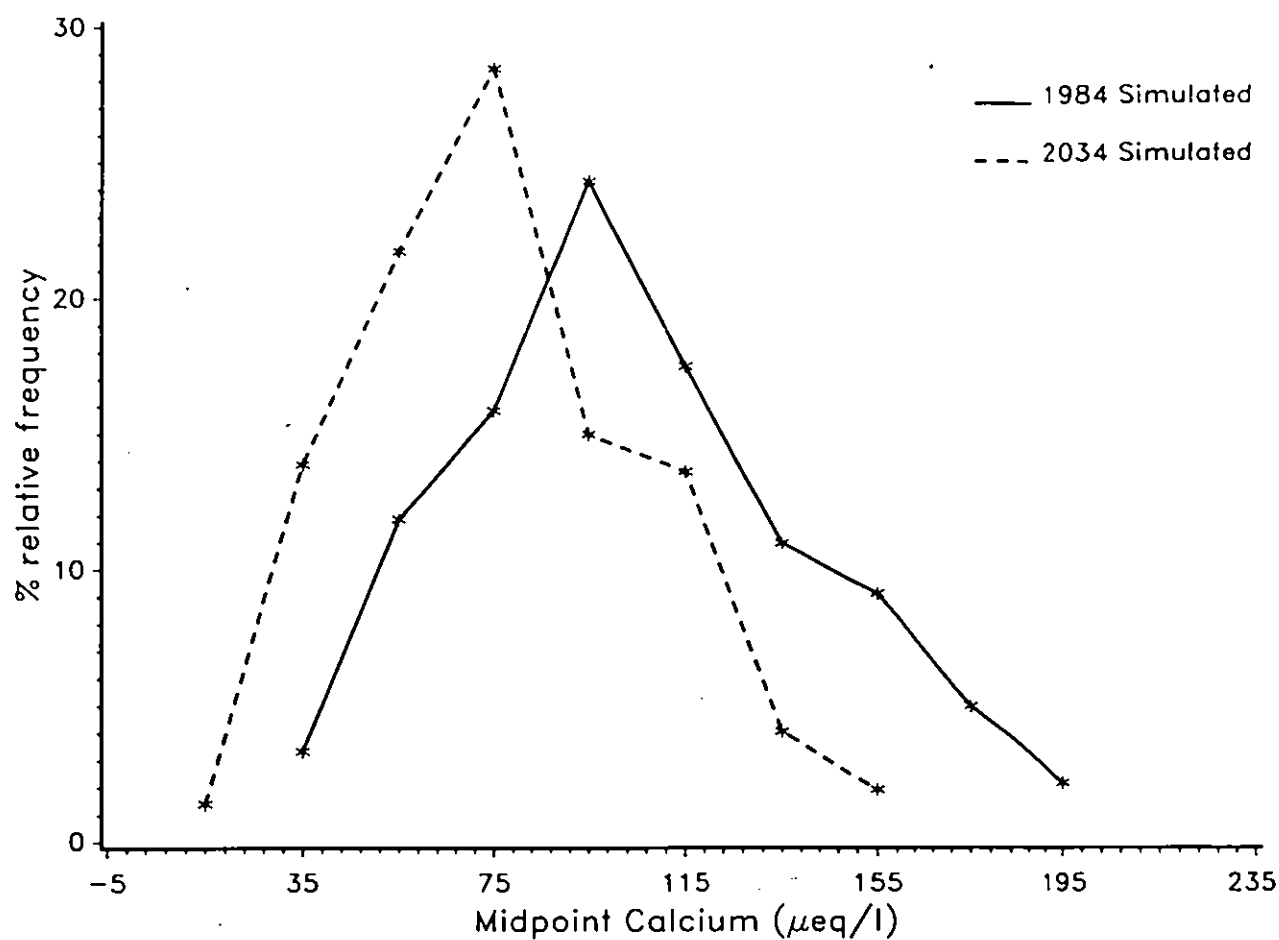
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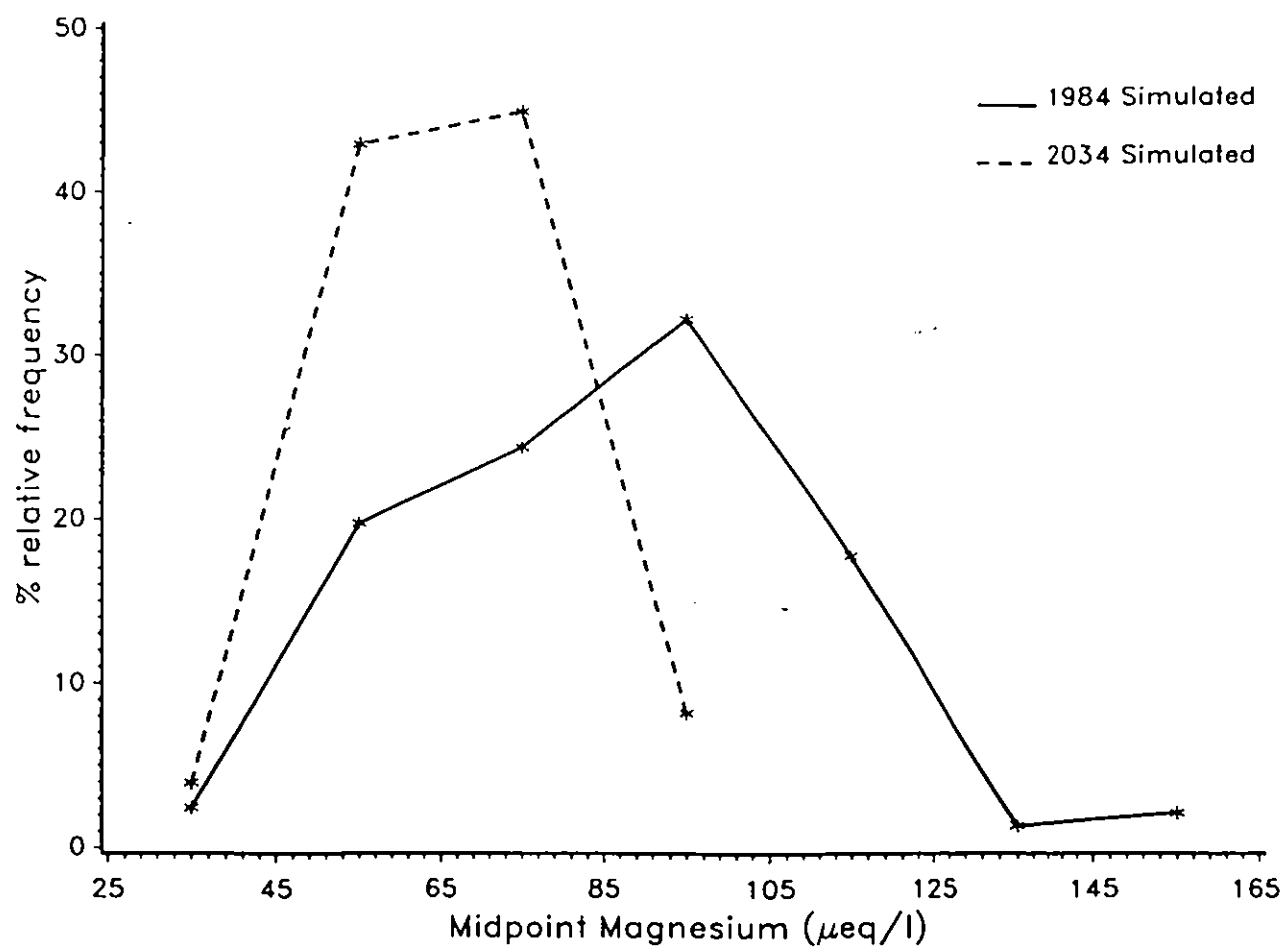
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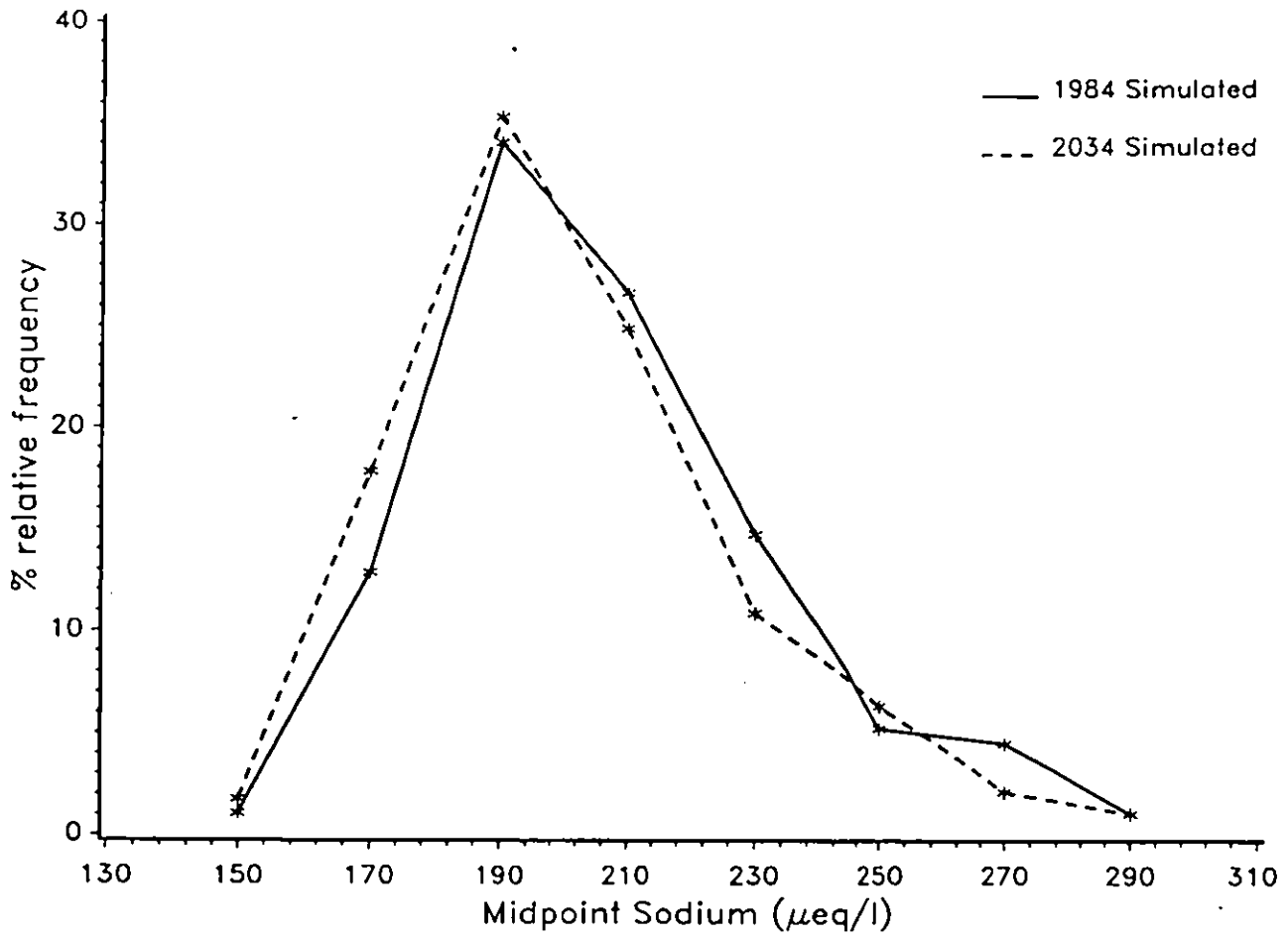


MAGNESIUM



SODIUM

Figure D6 (g)



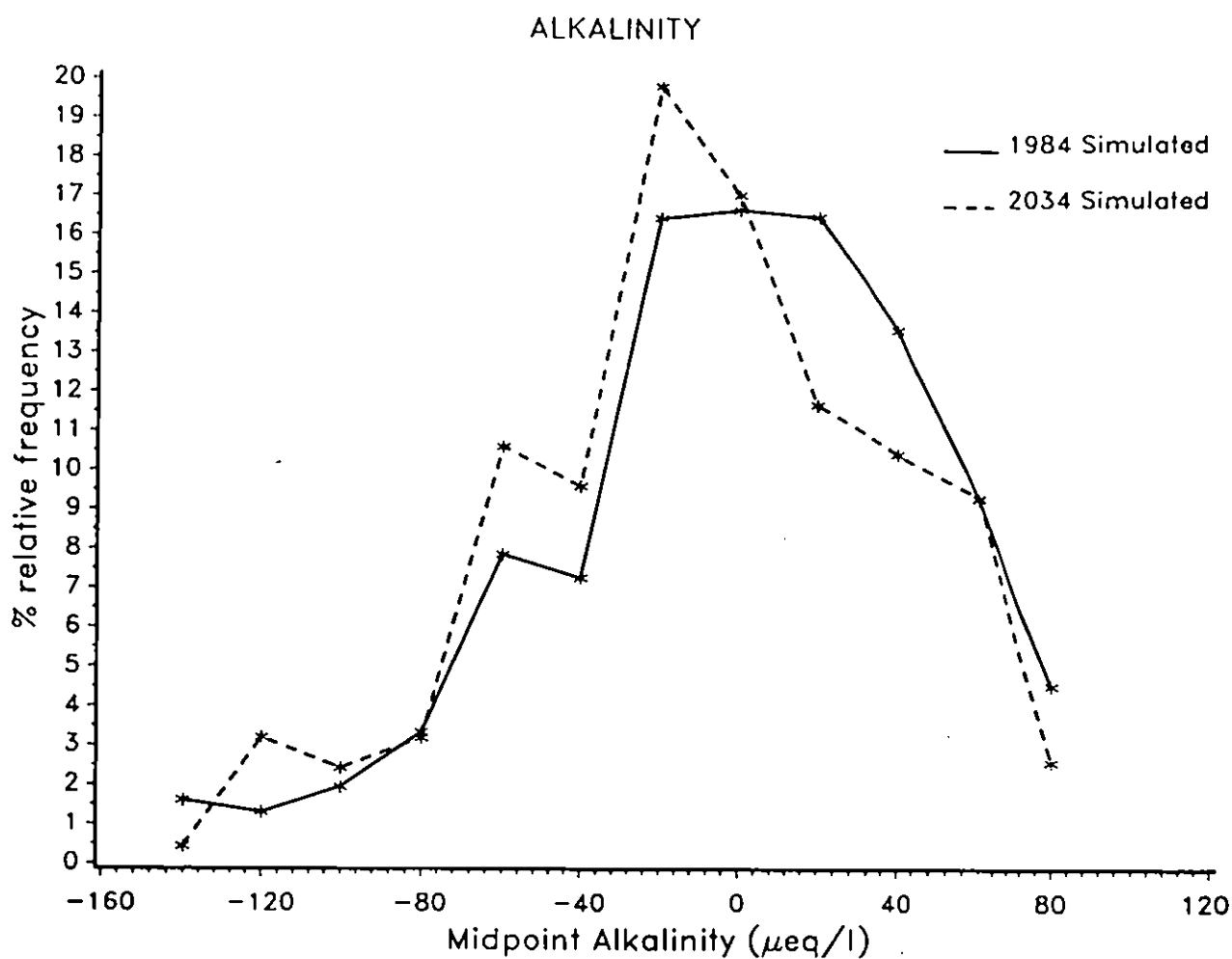
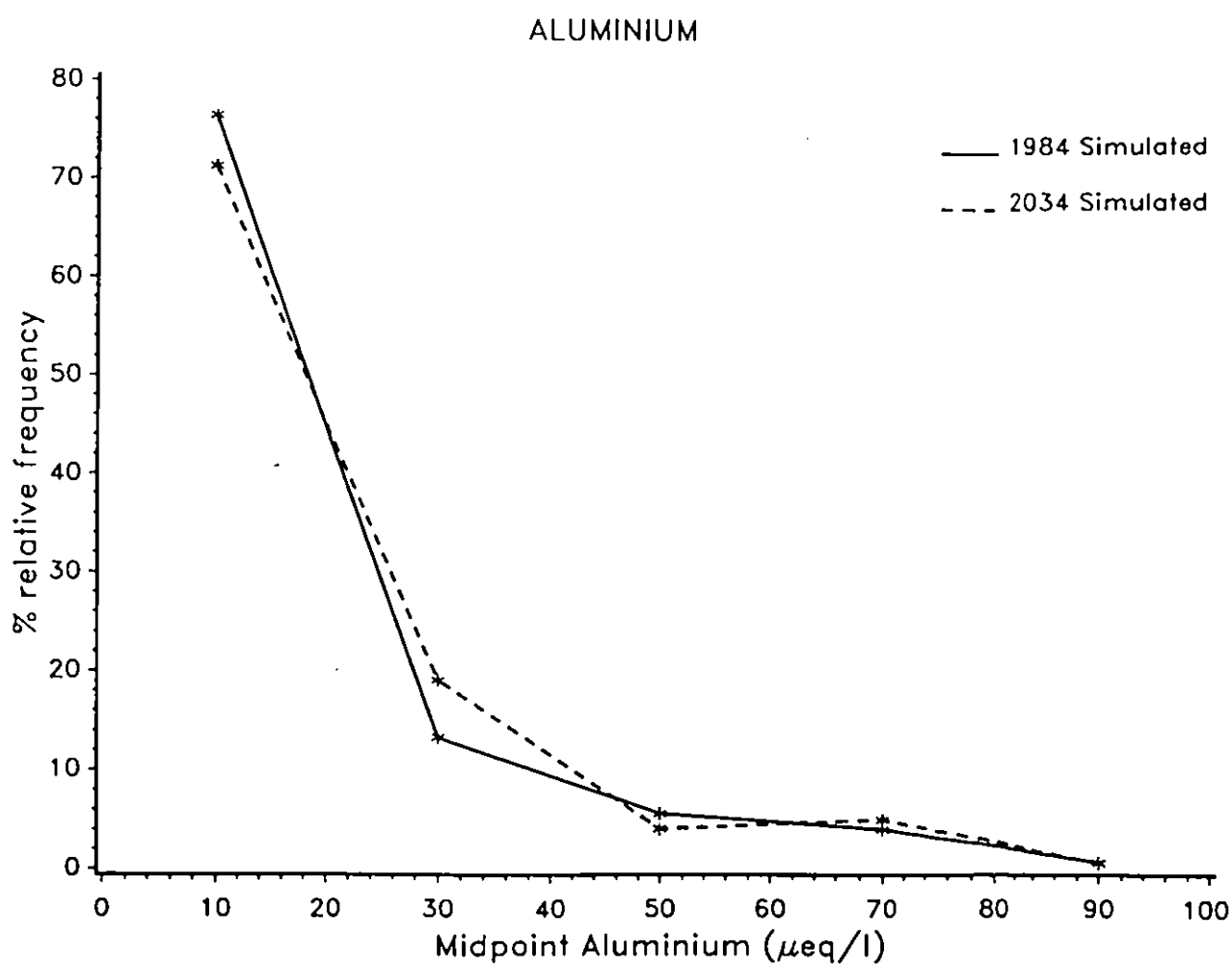


Figure D6 (b)



HYDROGEN

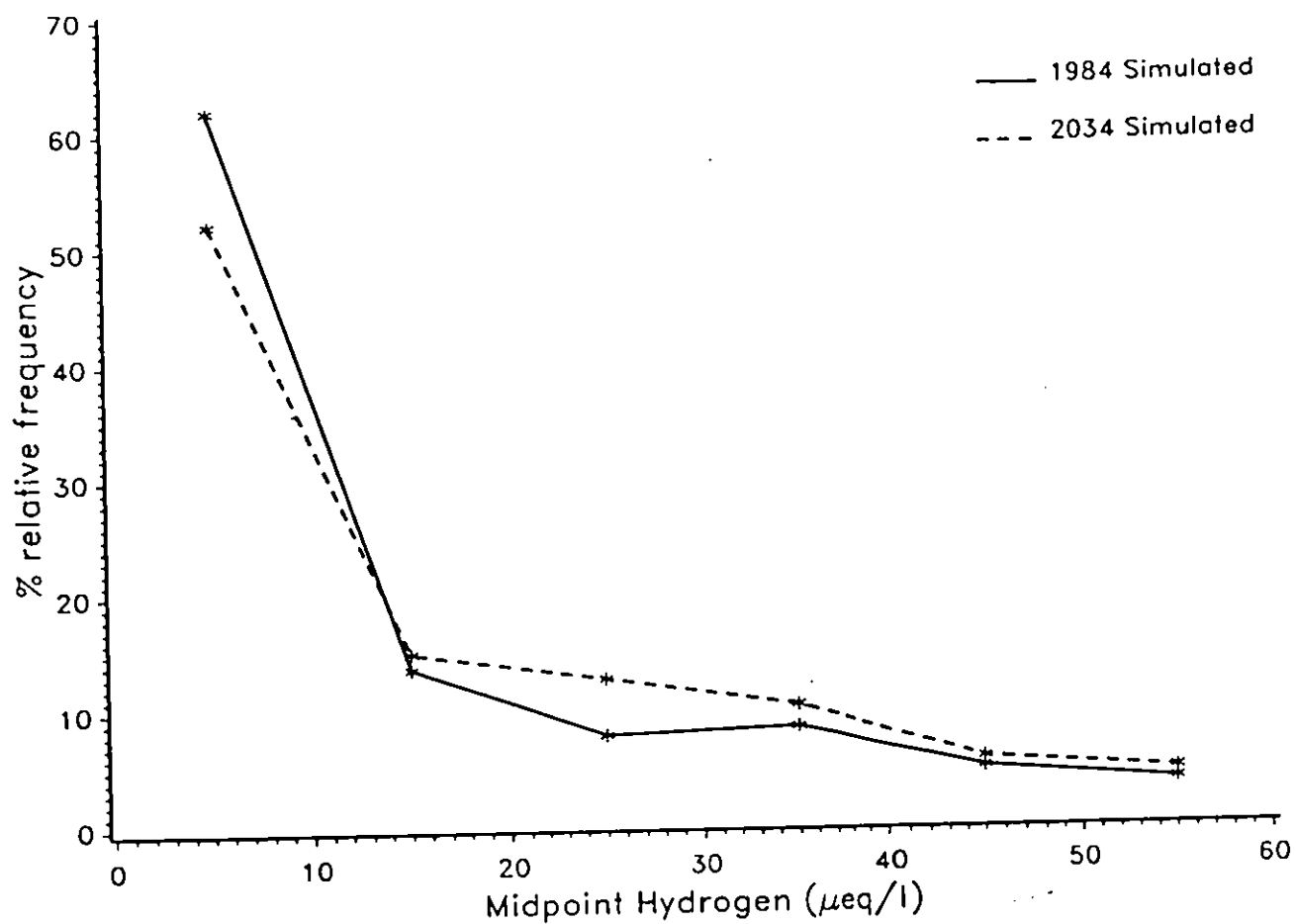
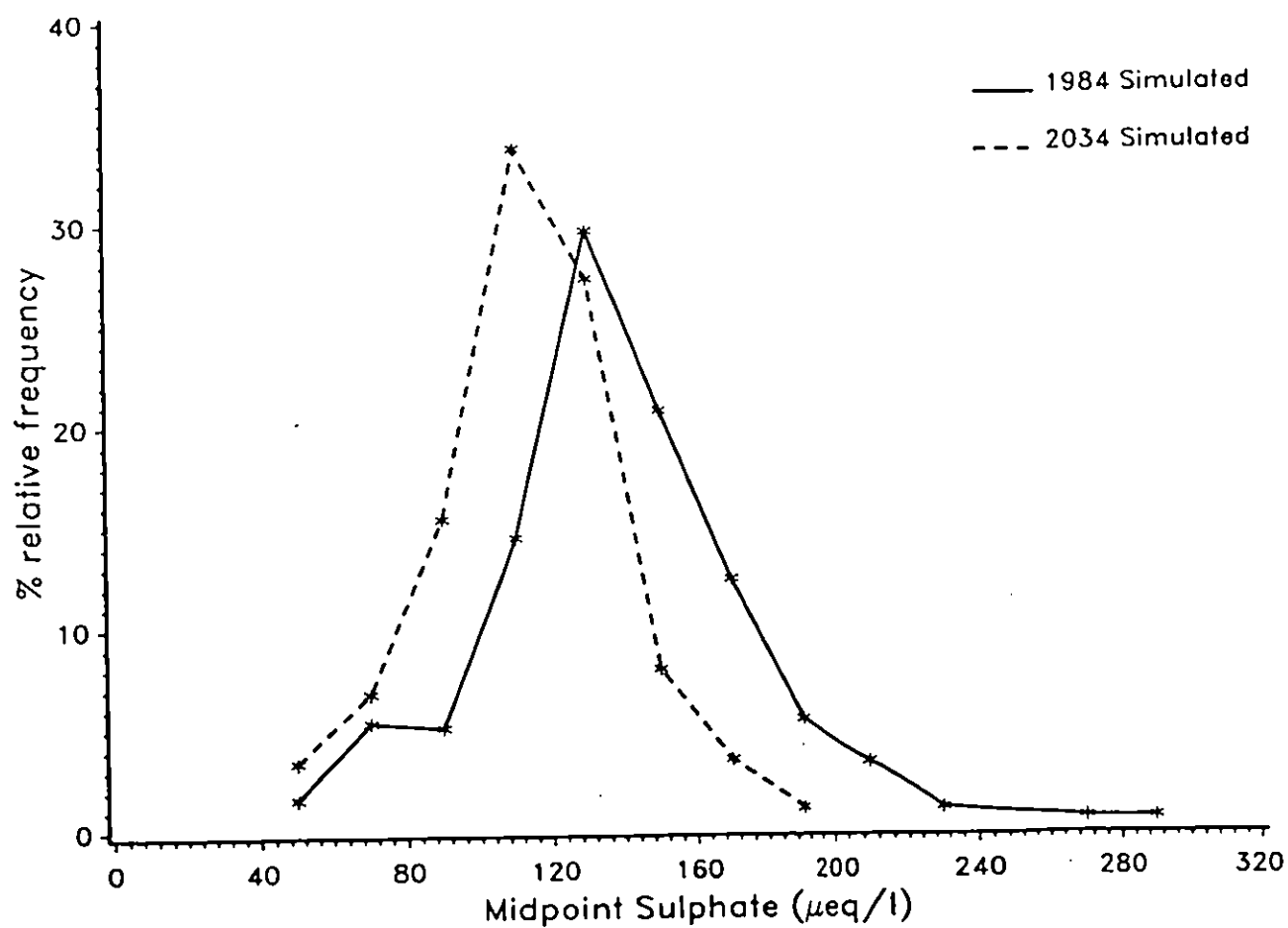


Figure D6 (d)

SULPHATE



CALCIUM

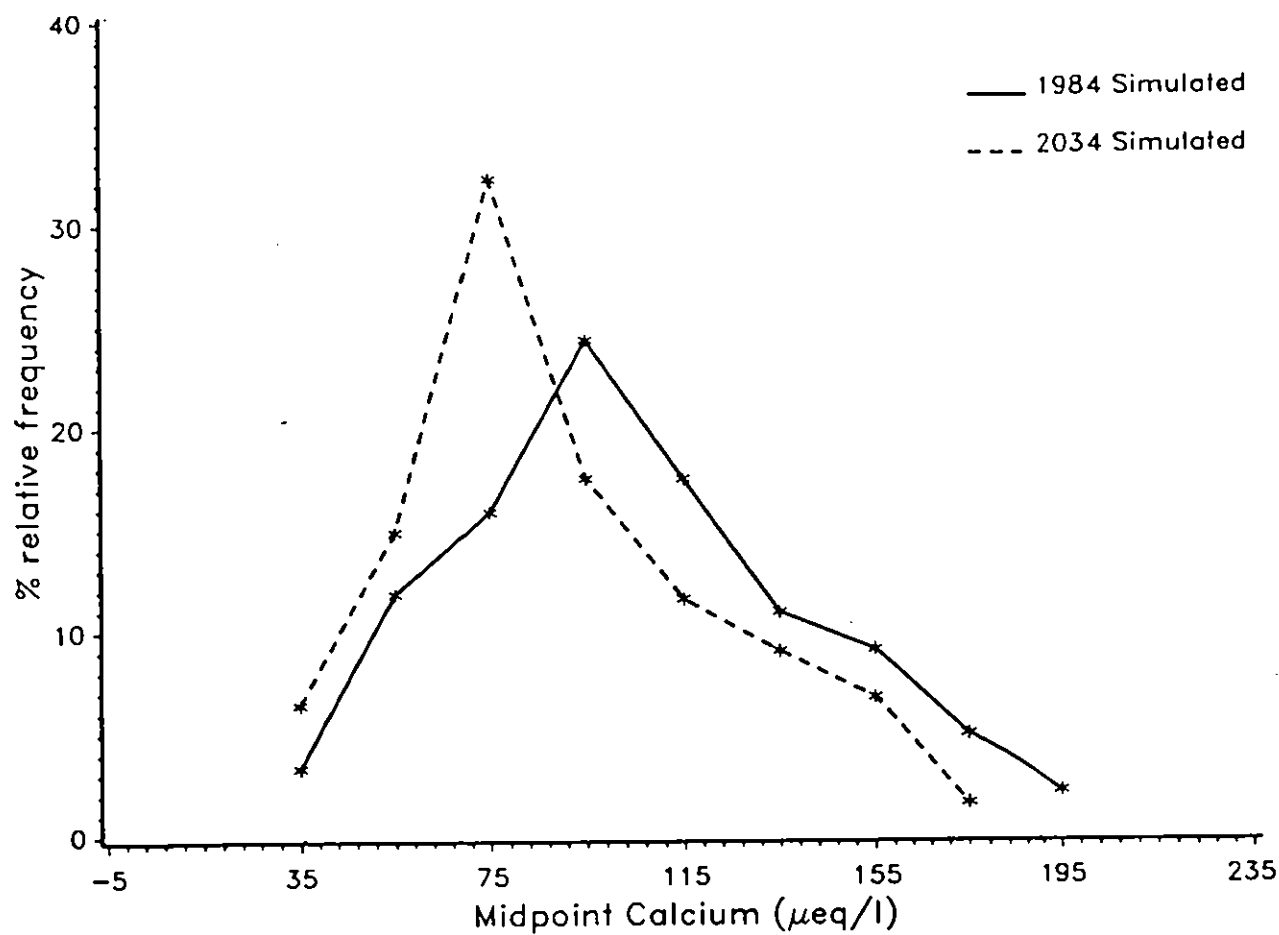
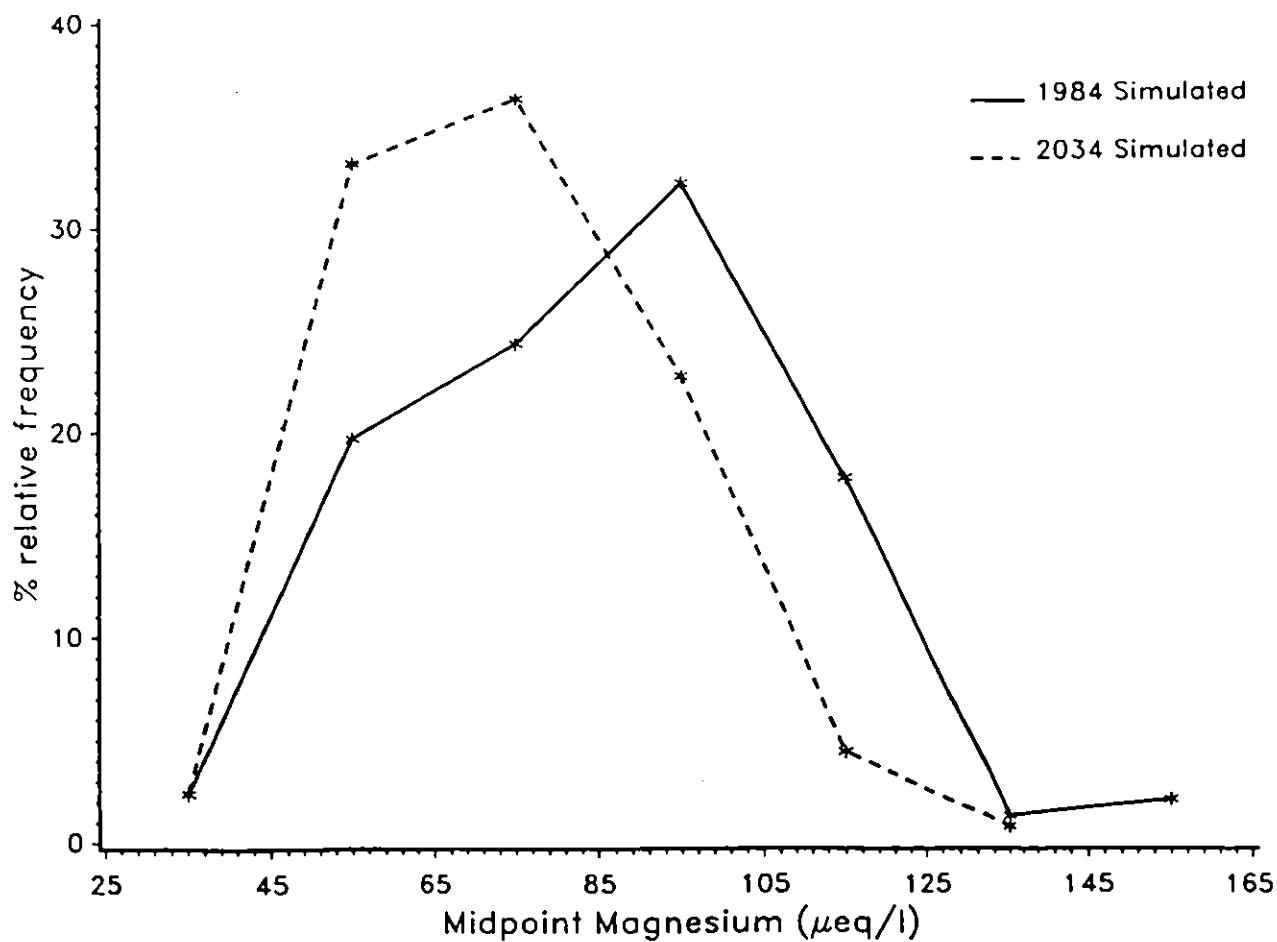


Figure D6 (f)

MAGNESIUM



SODIUM

